U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-274 115

Environmental Assessment of PCBs in the Atmosphere

MITRE Corp, McLean, Va

Prepared for

Environmental Protection Agency, Research Triangle Park, N C

Apr 76

PB 274 115

EPA-450/3-77-045

November 1977

ENVIRONMENTAL ASSESSMENT OF PCBs IN THE ATMOSPHERE

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

279

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-450/3-77-045

2.

3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE
Environmental Assessment of PCBs in the Atmosphere

5. REPORT DATE
April 1976

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
B. Fuller, J. Gordon, and M. Kornreich

8. PERFORMING ORGANIZATION REPORT NO.
MTR-7210 Rev. 1

9. PERFORMING ORGANIZATION NAME AND ADDRESS
MITRE Corporation
1820 Dolly Madison Blvd.
McLean, VA 22101

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
68-02-1495

12. SPONSORING AGENCY NAME AND ADDRESS
U.S. Environmental Protection Agency
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE
200/04

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This report examines atmospheric aspects of environmental problems associated with polychlorinated biphenyls (PCB). Subjects covered include: (1) physical and chemical properties of PCB, (2) monitoring methods for PCB in air, (3) sources of PCB emissions, (4) environmental distribution, transport, and transformation of PCB, (5) methods of control of PCB emissions, and (6) biological effects of PCB.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Chlorohydrocarbons	Carcinogens	Polychlorinated biphenyls	
Air Pollution	Capacitors	Askarels	
Physiological Effects	Transformers	Stationary Sources	
Industrial Plants	Ecology	Monitoring	
Air Pollution Control			

18. DISTRIBUTION STATEMENT
Unlimited

19. SECURITY CLASS *(This Report)*
Unclassified

20. SECURITY CLASS *(This page)*
Unclassified

21. NO. OF PAGES
279

22. PRICE
PCA13/MF A01

EPA Form 2220-1 (9-73)

EPA-450/3-77-045

ENVIRONMENTAL ASSESSMENT OF PCBs IN THE ATMOSPHERE

by

B. Fuller, J. Gordon, and M. Kornreich

The Mitre Corporation
McLean, Virginia

Contract No. 68-02-1495

EPA Project Officer: Donald Lokey

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

November 1977

1a

This report is issued by the Environmental Protection Agency to report technical data of interest to a limited number of readers. Copies are available free of charge to Federal employees, current contractors and grantees, and nonprofit organizations - in limited quantities - from the Library Services Office (MD-35), Research Triangle Park, North Carolina 27711; or, for a fee, from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161.

This report was furnished to the Environmental Protection Agency by The Mitre Corporation, McLean, Virginia, in fulfillment of Contract No. 68-02-1495. The contents of this report are reproduced herein as received from The Mitre Corporation. The opinions, findings, and conclusions expressed are those of the author and not necessarily those of the Environmental Protection Agency. Mention of company or product names is not to be considered as an endorsement by the Environmental Protection Agency.

Publication No. EPA-450/3-77-045

ABSTRACT

Polychlorinated biphenyls (PCBs) are highly toxic compounds whose large scale use over the years in numerous and diverse applications has resulted in their ubiquitous distribution throughout the environment. Since 1970, domestic sales of PCBs have been restricted to closed system electrical applications where no suitable replacement as an insulating fluid has been found. Imported PCBs are, however, presently used for dispersive applications, especially by the investment casting industry.

Loss of PCBs to the environment may occur during their production, transport, storage, incorporation into products, use and disposal. Due to evaporation and codistillation, loss to the atmosphere is possible whenever loss to the hydrosphere or lithosphere takes place. The highest levels of PCBs in both the atmosphere and hydrosphere occur close to urban and/or industrial centers. PCBs have been discovered in areas far removed from their points of origin and atmospheric transport represents the major pathway by which PCBs are disseminated throughout the world.

Although human exposure to PCBs is mainly through the diet, PCBs will be inhaled whenever they exist in the atmosphere. They are readily absorbed by both routes and accummulate in body tissue. In mammals, the major site of toxic action is the liver, although severe dermal effects, sensory nerve involvement, teratogenicity and carcinogenicity have also been reported.

Although the possibility of accidental release to the environment will continue to pose a threat as long as PCBs remain in use, the implementation of available control technology and proper disposal methods can minimize such losses.

ACKNOWLEDGEMENTS

We gratefully acknowledge our colleagues L. Thomas, R. Ouellette and J. Golden for their many helpful suggestions and criticisms. In addition, we wish to thank M. Jones and D. Lokey of the U.S. Environmental Protection Agency for their support and assistance.

TABLE OF CONTENTS

PAGE

I. CONCLUSIONS, RECOMMENDATIONS, AND SUMMARY 1-1

- A. Conclusions and Recommendations 1-1
- B. Summary 1-4

II. PHYSICAL AND CHEMICAL PROPERTIES 2-1

- A. Summary
- B. General Description and Physical Properties 2-2
- C. Specific Chemical Properties 2-16

III. METHODS FOR SAMPLING AND ANALYSIS OF POLYCHLORINATED BIPHENYLS IN THE ATMOSPHERE 3-1

- A. Summary 3-1
- B. Introduction 3-2
- C. Sampling for PCBs in the Atmosphere 3-4
  - 1. Liquid Absorption Methods 3-4
  - 2. Liquid Phases on Solid Supports 3-9
  - 3. Solid Adsorbents 3-16
- D. Extraction and Cleanup Procedures 3-20
- E. Qualitative and Quantitative Analysis 3-22
- F. Confirmation 3-26

IV. SOURCES 4-1

- A. Summary 4-1
- B. Production and Use 4-2
  - 1. Production 4-2
  - 2. Import and Export 4-9
  - 3. Uses and Replaceability 4-10
- C. Losses to the Environment 4-24
  - 1. Losses During Production, Transport, and Storage 4-24
  - 2. Losses During Use 4-25
  - 3. Disposal 4-34

V. MEDIA DISTRIBUTION, TRANSFORMATION, AND TRANSPORT 5-1

- A. Summary 5-1
- B. Atmosphere 5-2
- C. Hydrosphere and Lithosphere 5-14

TABLE OF CONTENTS (CONTINUED)

PAGE

D. Transport at Interfaces 5-35
  1. Air/Water Interface (including precipitation) 5-35
  2. Air/Soil Interface 5-46
  3. Soil/Water Interface (including sediment) 5-50
E. Transport Models 5-62

VI. CONTROL OF PCBs IN THE ATMOSPHERE 6-1

A. Summary 6-1
B. Introduction 6-2
C. Control of PCB Losses at Production Facilities and by Consumer Industries 6-3
  1. Methods for Control of Worker Exposure 6-3
  2. Methods for Control of External Emissions 6-6
D. Control of PCB Losses in Use 6-12
  1. Losses to Atmosphere 6-12
  2. Losses to Lithsophere 6-13
  3. Losses to Hydrosphere 6-16
E. Control of PCB Losses in Disposal 6-17
  1. Losses to Atmosphere 6-20
  2. Losses to Lithosphere 6-22
  3. Losses to Hydrosphere 6-23
F. Recommendations in Control Strategies 6-24
  1. Losses to Atmosphere 6-25
  2. Losses to Lithosphere 6-25
  3. Losses to Hydrosphere 6-26

VII. ENVIRONMENTAL EFFECTS OF PCBs 7-1

A. Summary 7-1
B. Effects on Humans and Laboratory Animals 7-1
  1. Absorption and Accumulation 7-1
  2. Metabolism and Elimination 7-5
  3. Lethality 7-6
  4. Toxic Effects on Liver 7-6
  5. Effects on Epithelium 7-8
  6. Hematological Effects 7-13
  7. Nervous System Effects 7-14
  8. Carcinogenesis 7-15
  9. Teratogenesis and Other Reproductive Effects 7-16
C. Other Environmental Effects 7-18
  1. Introduction 7-18
  2. Microorganisms 7-18
  3. Aquatic Organisms 7-19

TABLE OF CONTENTS (CONCLUDED)

PAGE

4. Birds 7-20
5. Mammalian Wildlife 7-21
6. Role of Trace Contaminants in Toxicity of Commercial PCB Mixtures 7-23

VIII. REFERENCES 8-1

LIST OF TABLES

TABLE NUMBER		PAGE
2.1	TYPICAL PERCENT COMPOSITION OF SOME POLYCHLORINATED BIPHENYL PRODUCTS	2-4
2.2	PHYSICAL PROPERTIES OF VARIOUS AROCLOR MIXTURES	2-6
2.3	ELECTRICAL PROPERTIES OF SOME AROCLORS	2-9
2.4	SOLUBILITY OF CHLOROBIPHENYLS IN WATER	2-10
2.5	THE SOLUBILITIES OF AROCLOR MIXTURES, 20°C	2-12
2.6	RELATIVE GAS CHROMATOGRAPH PEAK HEIGHTS (PEAK 5-100) IN SATURATED AQUEOUS SOLUTIONS OF AROCLOR 1254	2-13
2.7	APPROXIMATE VAPOR PRESSURE OF AROCLOR PREPARATIONS	2-15
2.8	PERCENT LOSS IN AREA OF SEVEN CHROMATOGRAPH PEAKS OF AROCLOR 1254 AFTER HEATING ON A STEAM BATH	2-17
2.9	PHOTO PRODUCTS OF IRRADIATION OF SIX TETRACHLOROBIPHENYLS IN HEXANE AND METHANOL	2-21
3.1	LIQUID PHASES ON SOLID SUPPORTS	3-11
3.2	CUMULATIVE AVERAGE QUANTITIES OF AROCLOR 1254 COLLECTED OVER AN 8-DAY PERIOD ON FOUR SETS OF COLLECTION PLATES SAMPLED AT DIFFERENT FREQUENCIES	3-14
3.3	SOLID ADSORBENT SAMPLING MEDIA	3-17
3.4	SYSTEMS FOR THIN-LAYER CHROMATOGRAPHY OF PCBs	3-27
4.1	THE WORLD'S MAJOR PRODUCERS OF PCBs	4-3
4.2	PCB MANUFACTURE AND SALES BY GRADE	4-5
4.3	U.S. EXPORT SALES OF PCBs BY MONSANTO 1963-1974	4-11
4.4	THE USES OF PCB PRIOR TO 1970	4-13

LIST OF TABLES (CONTINUED)

TABLE NUMBER PAGE

4.5 PCB MANUFACTURE AND SALES BY CATEGORY 4-14

4.6 PCB RESIDUES (PPM) IN SILAGE 4-28

4.7 PCB CONCENTRATIONS IN INDUSTRIAL EFFLUENTS 4-39

4.8 CONCENTRATION OF PCBs IN MUNICIPAL SEWAGE TREATMENT PLANT OUTFALLS 4-40

4.9 PCB CONCENTRATIONS IN WISCONSIN TREATMENT PLANT EFFLUENTS 4-42

4.10 PCB CONCENTRATIONS IN SLUDGE AND EFFLUENT FROM AN EXPERIMENTAL BIOLOGICAL OXIDATION SYSTEM 4-45

4.11 CONCENTRATIONS OF PCB (μg/1 as Aroclor 1254) IN SOME RIVER SYSTEMS 4-48

4.12 CONCENTRATION OF PCBs IN SEWAGE SLUDGES 4-50

5.1 AVERAGE MONTHLY LEVELS OF PCB IN AIRBORNE FALLOUT COLLECTED IN SOUTH SWEDEN (ng m^{-2} $month^{-1}$) 5-8

5.2 CONCENTRATIONS OF POLYCHLORINATED BIPHENYLS IN MARINE AND CONTINENTAL AIR 5-11

5.3 PCB CONCENTRATIONS OVER THE WESTERN NORTH ATLANTIC 5-13

5.4 ESTIMATED ANNUAL MASS EMISSION RATES OF POLYCHLORINATED BIPHENYLS TO THE SOUTHERN CALIFORNIA BIGHT (kg/yr) 5-17

5.5 SUMMARY OF PCB RESIDUE DATA FOR SURFACE AND GROUND WATER, JANUARY 1971 - JUNE 1972 5-23

5.6 CONCENTRATION AND ENRICHMENT FACTORS OF POLYCHLORINATED BIPHENYLS (AS AROCLOR 1254) IN SURFACE MICROLAYER SAMPLES FROM NARRAGANSETT BAY, RHODE ISLAND 5-27

LIST OF TABLES (CONCLUDED)

TABLE NUMBER		PAGE
5.7	POLYCHLORINATED BIPHENYLS (AS AROCLOR 1260) IN SARGASSO SURFACE MICROLAYER (SM) AND SUBSURFACE WATER (SS)	5-29
5.8	CONCENTRATIONS OF PCBs IN NORTH ATLANTIC OCEAN WATER	5-31
5.9	THE FATE OF 0.1 ppm POLYCHLORINATED BIPHENYL (AROCLOR 1260) IN 150 ml WATER SAMPLES FROM THE FRASER RIVER, THE NICOMEKL RIVER, AND GEORGIA STRAIT HELD IN THE LABORATORY FOR 12 WEEKS AT THE GIVEN TEMPERATURE	5-41
5.10	EVAPORATION PARAMETERS AND RATES FOR VARIOUS AROCLORS AT 25°C	5-44
5.11	FATE OF 0.1 ppm AROCLOR 1260 IN 150 ml WATER SAMPLES FROM FRASER RIVER AND FROM GEORGIA STRAIT IN THE PRESENCE OF BOTTOM SEDIMENTS FROM THE SAME SOURCES, INCUBATED AT 13°C	5-54
5.12	POLYCHLORINATED BIPHENYL CONCENTRATIONS (parts per billion (ppb) of the dry weight) IN DATED SEDIMENTS	5-56
5.13	PCB RESIDUES FOUND IN SAN FRANCISCO BAY AREA STREAMS	5-60
5.14	SUMMARY OF PCB RESIDUE DATA FOR BOTTOM SEDIMENTS, JANUARY 1971-JUNE 1972	5-61
5.15	GROSS ESTIMATES OF RATES IN INPUT AND ACCUMULATION OF PCBs IN NORTH AMERICA IN 1970	5-65
5.16	PCB ACCUMULATION BETWEEN 1930 AND 1970	5-71
6.1	FACILITIES AND SERVICES FOR PCB DISPOSAL	6-18
7.1	SYMPTOMS OF YUSHO PATIENTS (89 MALES, 100 FEMALES, AS OF OCTOBER 31, 1968)	7-10

LIST OF FIGURES

FIGURE NUMBER		PAGE
1.1	ACKNOWLEDGED ROUTES OF PCBs INTO THE ENVIRONMENT PRIOR TO 1970	1-9
1.2	PRESENT ACKNOWLEDGED ROUTES OF PCBs INTO THE ENVIRONMENT	1-11
1.3	ESTIMATED MOVEMENT OF PCBs THROUGH THE ENVIRONMENT	1-16
2.1	THE MOST COMMON SUBSTITUTION PATTERNS FOR THE CHLOROBIPHENYLS FOUND IN PCB PREPARATIONS	2-5
2.2	VAPOR PRESSURE OF DIFFERENT AROCLOR PREPARATIONS	2-14
3.1	FILTER, IMPINGER, AND ADSORPTION SAMPLING TRAIN	3-6
3.2	A TYPICAL FRITTED-GLASS BUBBLER USED IN SAMPLING FOR GASES	3-8
3.3	RECOVERY OF AROCLOR 1242 FROM SPIKED GLASS PLATE	3-15
3.4	HIGH VOLUME SAMPLER MODIFIED FOR HOLDING SOLID MEDIA	3-19
3.5	COMPARISON OF ELECTRON CAPTURE CHROMATOGRAMS FOR AROCLOR 1221, 1242, 1248, 1254, and 1260	3-25
3.6	PARTIAL MASS SPECTRA (GC-MS) OF AROCLOR 1254 SHOWING THE NUMBER OF CHLORINE ATOMS ON EACH ION	3-29
4.1	U.S. DOMESTIC SALES OF PCBs BY GRADE	4-7
4.2	U.S. DOMESTIC SALES OF PCBs BY APPLICATION	4-16
4.3	HOURLY CONCENTRATIONS OF POLYCHLORINATED BIPHENYLS IN THE INFLUENT AND EFFLUENT FROM THE CEDARBURG, WISCONSIN, TREATMENT PLANT, APRIL 15, 1971.	4-43

LIST OF FIGURES (CONCLUDED)

FIGURE NUMBER		PAGE
5.1	THE LOCATION OF SAMPLING STATIONS FOR THE DETERMINATION OF PCB RESIDUES IN AIRBORNE FALLOUT	5-7
5.2	SAMPLING SITES OVER THE WESTERN NORTH ATLANTIC	5-12
5.3	RELATIONSHIP OF ATMOSPHERIC PCB AND DISTANCE FROM INDUSTRIAL SOURCES	5-15
5.4	CONCENTRATION OF PCB IN SOIL WITH DISTANCE (ppm)	5-36
5.5	LOSS OF AROCLOR 1254 FROM ITSELF AS A FUNCTION OF TIME	5-48
5.6	LOSS OF AROCLOR 1254 FROM AN OTTAWA SAND	5-49
5.7	PERCENT DECREASE IN THE CONCENTRATION OF AROCLOR 1254 BY THE ADDITION OF INCREASING AMOUNTS OF ADSORBENT	5-52
5.8	DEPOSITION OF PCB IN DATED SEDIMENTS OF THE SANTA BARBARA BASIN	5-57
5.9	ENVIRONMENTAL TRANSPORT MODEL	5-64

I. CONCLUSIONS, RECOMMENDATIONS, AND SUMMARY

A. CONCLUSIONS AND RECOMMENDATIONS

Polychlorinated biphenyls (PCBs) are released to the atmosphere from a variety of sources. These include incomplete incineration and burning of PCB-containing wastes in municipal and private incinerators as well as in garbage dumps; vaporization from plasticizers, paints, and other PCB-containing coatings; vaporization from soil, sand, and other terrestrial reservoirs; evaporation and codistillation from natural bodies of water; and evaporation from their own surfaces when these have been exposed to the open air as in the case of accidental spillage, leaks, or wear and weathering of PCB-containing products. Loss to the atmosphere is, therefore, ultimately related to loss to other environmental compartments, and control of the former necessitates control of the latter.

PCBs, upon release to the atmosphere, are adsorbed to particulate matter and undergo transportation to areas far removed from their point of origin. They are eventually redeposited to the lithosphere and hydrosphere. As a result of aerial transport, an ever increasing accumulation of PCBs in the atmosphere will not take place. However, high atmospheric levels of PCBs may be expected to occur in urban industrialized areas, especially near incinerator stacks or garbage dumps. Unfortunately, only a limited amount of monitoring data is available for such areas. PCB levels over Providence, Rhode Island, in 1973 were as high as 9.4 nanograms (ng) per cubic meter (m^3), or approximately 1 part per trillion (ppt). However, levels on suspended particulates in four U.S. cities between 1968 and 1970 ranged from 27 to 230 micrograms (μg) PCBs per gram (g) of particulate, with a mean concentration of 50 μg/g of particulate. Assuming a particulate loading of 60 $\mu g/m^3$, this average amounts to 3 ng/m^3 PCBs. The extent to which release of PCBs into the atmosphere poses a threat to the general urban population remains uncertain due to the scarcity of data relating to the toxic effects of low-level PCB inhalation in mammals. In one inhalation study, 1.5 milligrams per cubic meter (mg/m^3; 0.11 parts per million [ppm]) of Aroclor 1254 was sufficient to produce noticeable changes in rat liver following exposure for several weeks. The maximum atmospheric concentration per 8-hour workday allowed by the American Conference of Governmental Industrial Hygienists (1973) for Aroclor 1254 is 0.5 mg/m^3 (0.037 ppm), one-third the level at which an effect was experimentally observed in rats. The standard for Aroclor 1242 is presently set at 1.0 mg/m^3 (0.094 ppm).

In view of the above stated facts, the following recommendations appear warranted:

1. Extensive monitoring data must be obtained for ambient PCB concentrations over urban areas. Emphasis should be placed on determination of levels near such possible sources as municipal incinerators, private incinerators operated by PCB-using industries, and garbage dumps.

2. Since most toxicity data relate to ingestion of PCBs, studies must be initiated that will elucidate, in detail, all toxic effects of low-level inhalation in mammals. Only by combining ambient levels with toxicity data may we come to a definite, meaningful conclusion concerning the health hazards of present atmospheric PCB levels.

3. From what little is known about toxic effects at low atmospheric concentrations, workplace standards should be reevaluated and acceptable concentration levels should perhaps be lowered.

4. Until definite toxicity data becomes available, the latest, most efficient control technology must be implemented, if necessary, through legal actions. High temperature incinerators (operated above 2000°F) will completely degrade PCBs to benign substances. Scrubbers should be required on those incinerators that do not reach the necessary temperatures. Scrubbers that remove particulates as well as gaseous effluents are available and are necessary. Mist eliminators (such as the Brink Mist Eliminator used by Monsanto) may be installed in vapor lines to condense and collect vapors in the plant. Carbon adsorption system (such as VentSorb from Calgon) may be hooked up to the vent of a storage tank or other point source and may, in addition, be adaptable to ventilation systems.

Numerous techniques for minimization of release to the hydrosphere are also available and are discussed in detail in the report that follows.

5. Available substitutes for PCBs, especially in electrical applications, should be considered. Two companies, Dow Corning and Dow Chemical, claim to have developed suitable substitutes for PCBs in transformers and capacitors, respectively. Dow Corning's substitute available for transformers is a polydimethyl siloxane liquid known as "200 fluid". It is thermally stable, less explosive than PCBs but is slightly more flammable. The substitute to be used on capacitors is an alkylated chlorodiphenyl oxide that Dow Chemical hopes to commercialize by early 1976. Monsanto and General Electric (G.E.) are also working on substitute materials. The G.E. product, known as Econol, is based on a phthalate ester and is presently used in G.E. exports to Japan where PCBs are now banned.

B. SUMMARY

Polychlorinated biphenyls (PCBs) are substituted derivatives of the compound biphenyl in which anywhere from one to ten of the hydrogen atoms have been replaced by chlorine. PCBs are synthesized commercially as mixtures of isomers, with the largest proportion of component compounds corresponding in composition to the average chlorine content of the mixture. While most individual chlorobiphenyls are solids at room temperature, the majority of the commercial mixtures are mobile oils. The physical characteristics which render PCBs useful are their thermal stability, non-flammability and excellent dielectric properties. They are also resistant to acids, bases, oxidizing agents and other chemicals unless treated under vigorous reaction conditions. PCBs are soluble in most of the common organic solvents but are only slightly soluble in water. Aqueous solubility of both individual isomers and mixtures, in general, has been found to decrease with increasing chlorine content. Of the individual isomers studied, the one exhibiting the greatest solubility in water was 2-monochlorobiphenyl (5.9 ppm). The solubility of a commercial mixture containing 42 percent chlorine by weight was 200 parts per billion (ppb). Vapor pressures are also low and tend to parallel aqueous solubility with the preparations containing a higher percentage of less chlorinated isomers being most volatile. The vapor pressures of commerical mixtures containing 32 percent and 54 percent chlorine by weight are 5×10^{-3} millimeters of mercury (mm Hg), and 6×10^{-5} millimeters of mercury respectively. PCBs tend to adhere to smooth surfaces and are thus present in the environment adsorbed to sediment and transported via airborne particulates. One pathway by which they may be removed from the environment is through photochemical decomposition in the presence of sunlight. Reductive dechlorination is the major photochemical reaction. However, in hydroxylic solvents or aqueous suspension, replacement by alkoxy- or hydroxy groups also occurs. The ortho position is the preferred site of attack in both instances. Evidence suggests that highly toxic chlorodibenzofurans are formed from 2-chlorobiphenyls under photochemical conditions leading to the formation of oxygenated products. Since chlorodibenzofurans are themselves photolabile, their accumulation in the atmosphere as a byproduct of photochemical decomposition of PCBs is unlikely.

Sampling methods for atmospheric PCBs fall into three categories: liquid absorption systems, liquid phases on solid supports, and solid adsorbents. Liquid absorption systems are most popular, but are only suitable when high concentrations are expected. Liquid phases on solid supports are used primarily for static sampling when relative levels of contamination rather than ambient concentrations are sought. The most promising sampling material is polyurethane foam. Polyurethane foam is compatable with high volume collection, does away with the need for interfering collection liquids, and appears relatively specific for PCBs.

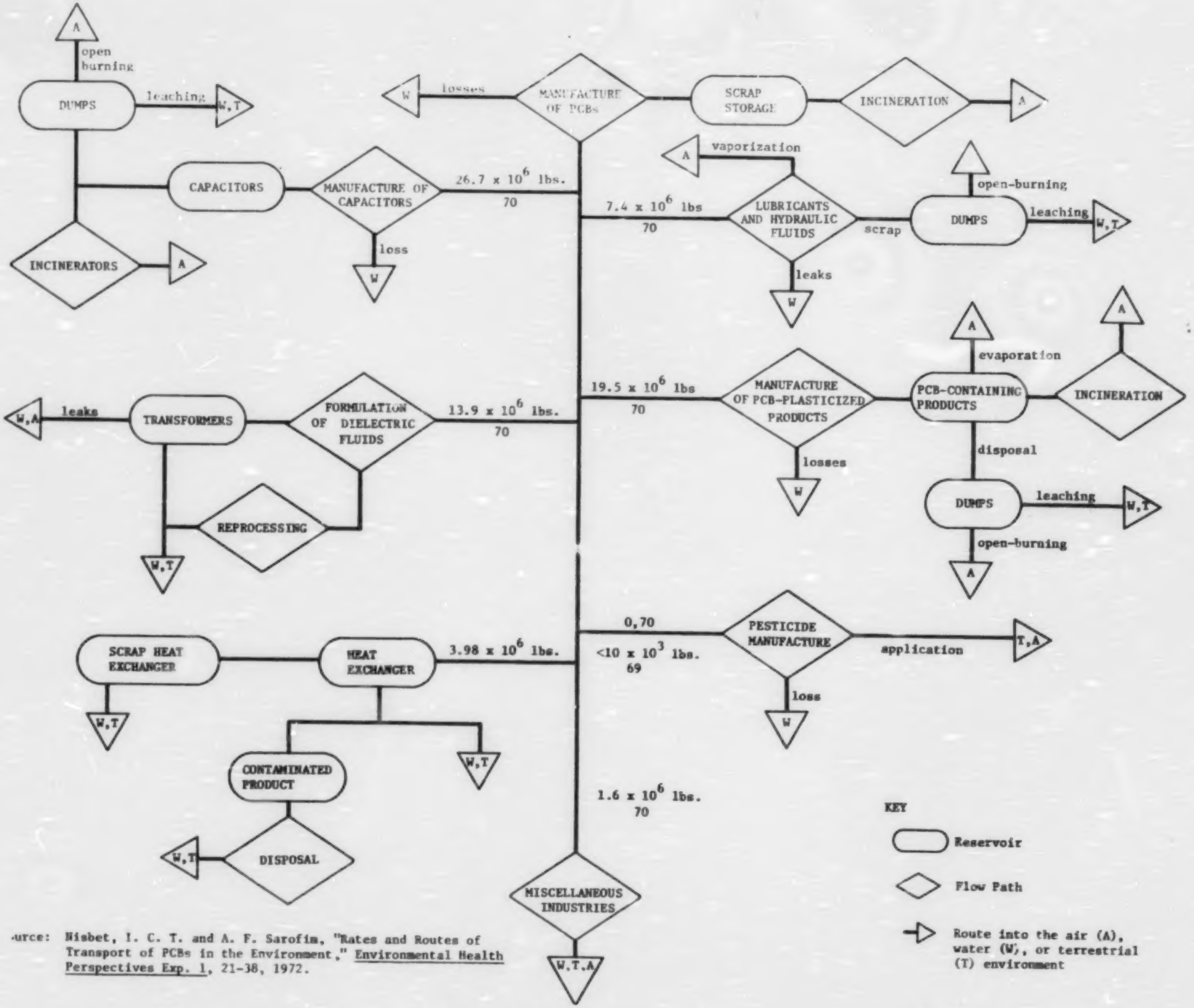
The most sensitive analytical method for PCBs is electron capture gas chromatography. Unequivocal qualitative confirmation may be obtained by mass spectrometry.

PCBs are manufactured commercially in many of the world's industrialized nations, although production has been banned in Japan since 1972. The sole producer of PCBs in the United States is the Monsanto Company, which markets its mixtures under the trade name "Aroclor." A voluntary restriction of sales to closed system electrical applications was initiated by Monsanto in 1970, resulting in a 50 percent decrease in production and sales by that company through 1974.

Prior to 1970, PCBs found use in a variety of applications which relied upon their unique chemical and thermal stability and electrical insulating properties. They were found, for example, in heat transfer fluids, hydraulic fluids, high vacuum oils, epoxy paints, printing inks, sealers in water-proofing compounds, and many other types of products. Their major use, however, was and continues to be as an insulating fluid in capacitors and transformers. Following the discovery of a wide range of adverse effects associated with the release of PCBs into the environment, an attempt was made to curb their use for dispersive applications through the aforementioned restriction of sales. However, the possibility that PCBs might be obtained for such applications from other sources (for example imports) continues to be of significant concern to environmentalists, especially since little evidence for a decrease in environmental levels of PCBs following the sales restrictions were found. Some environmentalists (such as William G. Turney of Michigan) feel that the only certain means of getting PCBs out of the environment may be to ban them completely, and several companies in anticipation of such action are seeking alternatives to PCBs for all types of applications, including electrical. For example, Dow Corning Company and Dow Chemical Company claim to have developed suitable substitutes for PCBs as insulating fluids in transformers and capacitors, respectively. Dow Corning's substitute available for transformers is a polydimethyl solixane liquid known as "200 fluid." It is thermally stable, less explosive than PCBs and only slightly more flammable. The substitute to be used in capacitors is an alkylated chlorodiphenyl oxide which Dow Chemical hopes to commercialize by early 1976.

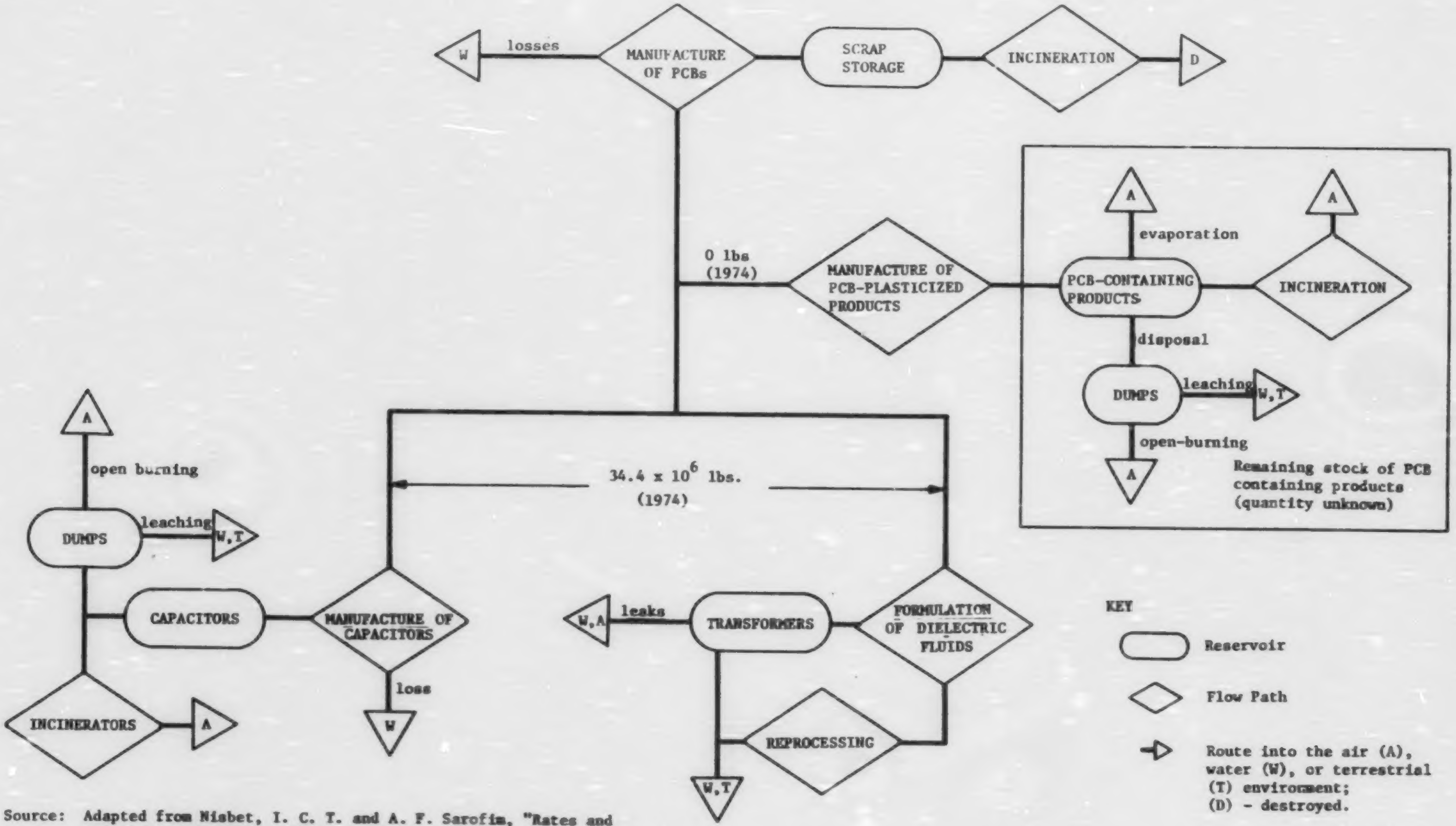
Loss of PCBs to the environment may occur during their production, transport, storage, incorporation into products, use, and disposal. Due to evaporation and codistillation, loss to the atmosphere is possible whenever loss to the hydrosphere or lithosphere takes place. The pathways by which PCBs entered the environment prior to 1970, and by which they are believed to enter the environment at present are summarized in Figures 1.1 and 1.2, respectively. Losses during production at the Monsanto facilities are presently estimated to be insignificant, resulting, for example, in a parts-per-trillion concentration in the effluent reaching the Mississippi River. Losses during transport and storage are mainly due to leaks and spills and are also thought to be small. Release to the environment as a consequence of use occurred maximally prior to 1970 and was, for the most part, unintentional. The major pathways by which PCBs were lost to the atmosphere, hydrosphere, lithosphere, and food supply during use included vaporization from PCB-containing paints, coatings and plastics; migration and leaching from surface coatings and packaging materials; leakage from faulty heat exchange systems and partially sealed hydraulic systems and burnout of PCB-containing ballasts in fluorescent light fixtures.

The primary source of PCBs in all compartments of the environment is undoubtedly the disposal of waste PCBs by consumer industries and of PCB-containing products by municipal treatment plants. Disposal practices which lead to environmental contamination include: (1)


A
open burning
DUMPS
leaching
W,T
CAPACITORS
INCINERATORS
A
MANUFACTURE OF CAPACITORS
loss
W
W
losses
MANUFACTURE OF PCBs
SCRAP STORAGE
INCINERATION
A
26.7 x 10^6 lbs.
70
7.4 x 10^6 lbs
70
A
vaporization
LUBRICANTS AND HYDRAULIC FLUIDS
leaks
W
scrap
DUMPS
open-burning
A
leaching
W,T
W,A
leaks
TRANSFORMERS
FORMULATION OF DIELECTRIC FLUIDS
13.9 x 10^6 lbs.
70
REPROCESSING
W,T
19.5 x 10^6 lbs
70
MANUFACTURE OF PCB-PLASTICIZED PRODUCTS
losses
W
PCB-CONTAINING PRODUCTS
evaporation
A
INCINERATION
A
disposal
DUMPS
leaching
W,T
open-burning
A
0,70
<10 x 10^3 lbs.
69
PESTICIDE MANUFACTURE
loss
W
application
T,A
SCRAP HEAT EXCHANGER
W,T
HEAT EXCHANGER
3.98 x 10^6 lbs.
W,T
CONTAMINATED PRODUCT
DISPOSAL
W,T
1.6 x 10^6 lbs.
70
MISCELLANEOUS INDUSTRIES
W,T,A
KEY
Reservoir
Flow Path
Route into the air (A), water (W), or terrestrial (T) environment

urce: Nisbet, I. C. T. and A. F. Sarofim, "Rates and Routes of Transport of PCBs in the Environment," Environmental Health Perspectives Exp. 1, 21-38, 1972.

FIGURE 1.1
ACKNOWLEDGED ROUTES OF PCBs INTO THE ENVIRONMENT PRIOR TO 1970


W
losses
MANUFACTURE OF PCBs
SCRAP STORAGE
INCINERATION
D
0 lbs (1974)
MANUFACTURE OF PCB-PLASTICIZED PRODUCTS
A
evaporation
PCB-CONTAINING PRODUCTS
INCINERATION
A
disposal
DUMPS
leaching
W,T
open-burning
A
Remaining stock of PCB containing products (quantity unknown)
34.4 x 10^6 lbs. (1974)
A
open burning
DUMPS
leaching
W,T
CAPACITORS
MANUFACTURE OF CAPACITORS
loss
W
INCINERATORS
A
W,A
leaks
TRANSFORMERS
FORMULATION OF DIELECTRIC FLUIDS
REPROCESSING
W,T
KEY
Reservoir
Flow Path
Route into the air (A), water (W), or terrestrial (T) environment;
(D) - destroyed.

Source: Adapted from Nisbet, I. C. T. and A. F. Sarofim, "Rates and Routes of Transport of PCBs in the Environment," Environmental Health Perspectives Exp. 1, 21-38, 1972.

FIGURE 1.2
PRESENTLY ACKNOWLEDGED ROUTES OF PCBs
INTO THE ENVIRONMENT

Preceding page blank

open burning or incomplete incineration of municipal and industrial solid wastes; (2) allowing PCB-containing fluids to flow into waterways with municipal and industrial water water effluents; (3) dumping of sewage sludge, solid waste, and dredge spoil at sea, and; (4) dumping of sewage sludge and solid waste into sanitary landfills and dumps.

Since PCBs vaporize unless incinerated at temperatures greater than 2000°F, loss to the atmosphere following destruction of PCB-containing refuse at municipal incinerators is very likely. Although no actual data on gaseous PCB emissions from municipal incinerator stacks are available, residues were detected in two samples of fly ash from such incinerators. Further studies dealing with incinerator emissions are needed.

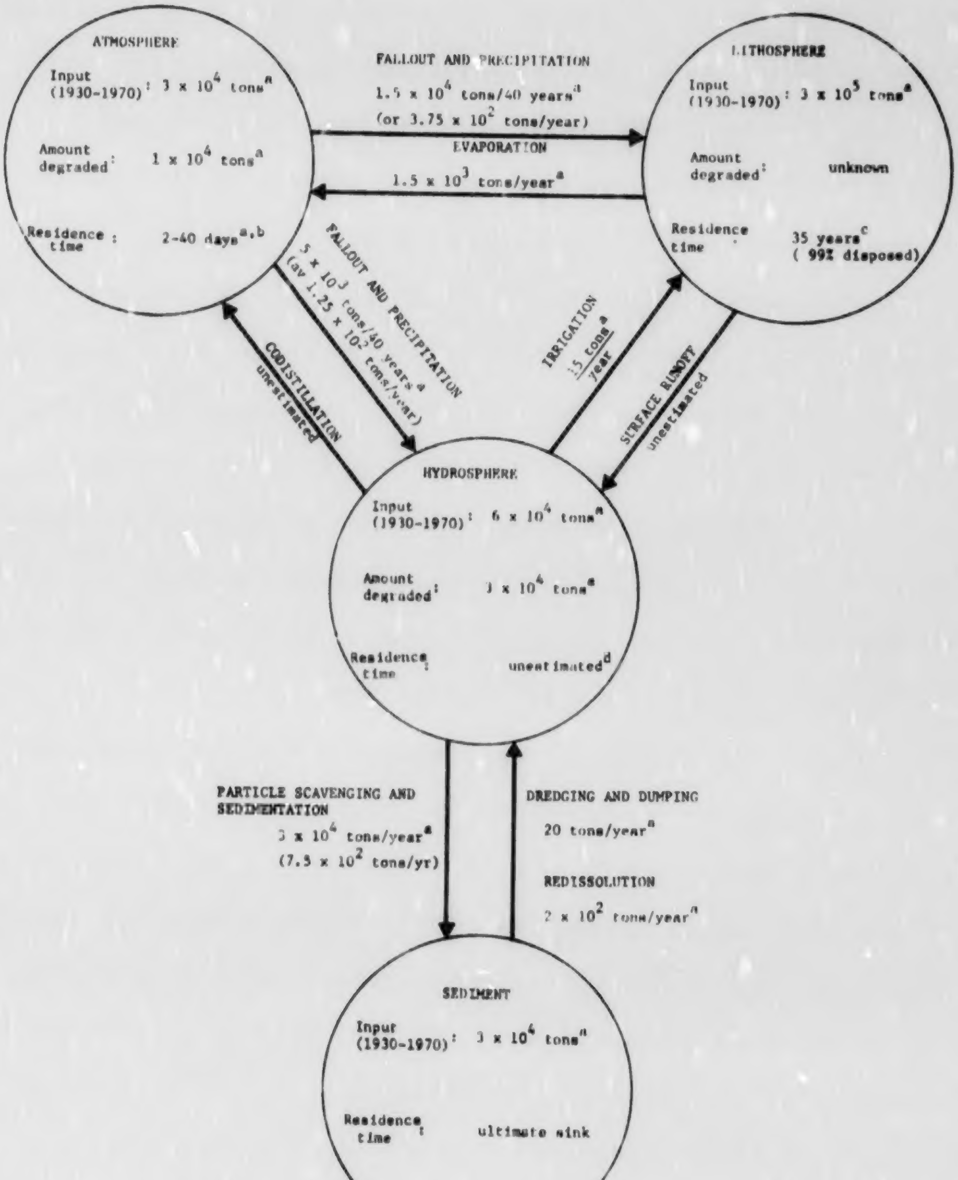
Discharge of PCB-containing effluents has resulted in serious contamination of several rivers and coastal waters. General Electric has admitted to dumping as much as 30 pounds of PCBs (13.62 kilograms, or kg) per day into the Hudson River, and effluents sampled from several industrial plants throughout the United States contained concentrations ranging from 2.5 to 275 parts-per-billion. Discharge into rivers from selected municipal sewage treatment outfalls ranged from 0.002 pounds (0.91 grams) to 213 pounds (96.7 kg) per day; municipal release has recently been found to be the primary source of PCBs in the marine ecosystem off Southern California. About 6.5 metric tons were discharged during 1973-1974.

Preceding page blank

As might be expected, the highest levels of PCBs in both the atmosphere and hydrosphere occur close to urban and/or industrial centers. In the atmosphere, PCBs may be found in the vapor phase, in the form of an aerosol, or adsorbed onto particulate matter. Levels of PCBs on suspended particulate in four U.S. cities between 1968 and 1970 ranged from 27 to 230 μg/g of particulate with a mean concentration of 50 μg/g of particulate. Assuming a particulate loading of 60 $\mu g/m^3$, this average amounts to 3 ng/m^3 PCBs. PCBs in dry aerial fallout within the Los Angeles Basin ranged from 7.8×10^{-8} gram/square meter/day to 1.7×10^{-6} g/m^2/day. PCBs, mainly in the vapor phase, were detected over the western North Atlantic. Concentrations were highest at sampling stations closest to the Boston-Hartford-New York-New Jersey industrial complex but decreased 100 fold at a station located 2000 kilometers (km) farther out to sea.

PCBs are found in the hydrosphere mainly adsorbed to particulate matter and sediment. Due to their lipophilic nature, high concentrations also tend to accumulate in the surface microlayer of the ocean. Due to low aqueous solubility, only small quantities are found naturally in solution. Actual concentrations observed in some fresh water systems range from 0.5 ppt for unpolluted waters (such as that in the Göto and Nordre Rivers in Sweden) to 15,800 ppt in the highly polluted Great Miami River in Ohio. Concentrations as high as 4.2 parts-per-billion (ppb) have been observed in the surface microlayer of Narragansett Bay, Rhode Island. Subsurface water from the same location contained 0.15 ppb.

The discovery of significant concentrations of PCBs in the atmosphere and hydrosphere far removed from urban industrial areas suggests that the atmosphere represents the major pathway by which PCBs are transported throughout the world. PCBs have also been detected in precipitation (such as antarctic snow) in support of this hypothesis. Analysis of accumulated evidence reveals a model in which the atmosphere plays a central role. PCBs released directly into the atmosphere adsorb onto particulates and are transported with the prevailing winds. Transport in the vapor phase may also occur. Particle fallout and precipitation deposit the PCBs onto land or into bodies of water. Most PCBs reaching the hydrosphere are removed by particle scavenging followed by sedimentation; a small amount remains dissolved and is subject to re-evaporation. This phenomenon is particularly noticeable in marine waters located in areas of high evaporation and low rainfall. But evaporation from shallow, fast-flowing streams fed with PCB-containing effluents may be significant enough to result in falsely diminished estimates of hydrospheric contamination. Successive cycles of evaporation, adsorption and deposition eventually carry the PCBs, initially released on land, to the coast and to their ultimate sink, the sediment of the oceanic abyss. A scheme depicting the movement of PCBs through the environment including quantitative estimates of the amounts of material involved at each step is presented in Figure 1.3. Due to differential vapor pressures, the majority of atmospheric samples analyzed contain a higher proportion of lower-chlorinated


ATMOSPHERE
Input (1930-1970): 3 x 10^4 tons^a
Amount degraded: 1 x 10^4 tons^a
Residence time: 2-40 days^a,b
FALLOUT AND PRECIPITATION
1.5 x 10^4 tons/40 years^a
(or 3.75 x 10^2 tons/year)
EVAPORATION
1.5 x 10^3 tons/year^a
LITHOSPHERE
Input (1930-1970): 3 x 10^5 tons^a
Amount degraded: unknown
Residence time: 35 years^c (99% disposed)
FALLOUT AND PRECIPITATION
5 x 10^3 tons/40 years^a
(av 1.25 x 10^2 tons/year)
CODISTILLATION
unestimated
IRRIGATION
15 tons^a/year
SURFACE RUNOFF
unestimated
HYDROSPHERE
Input (1930-1970): 6 x 10^4 tons^a
Amount degraded: 3 x 10^4 tons^a
Residence time: unestimated^d
PARTICLE SCAVENGING AND SEDIMENTATION
3 x 10^4 tons/year^a
(7.5 x 10^2 tons/yr)
DREDGING AND DUMPING
20 tons/year^a
REDISSOLUTION
2 x 10^2 tons/year^a
SEDIMENT
Input (1930-1970): 3 x 10^4 tons^a
Residence time: ultimate sink

a. Nisbet and Sarofim (1972)
b. Bidleman and Olney (1974a).
c. based on a half-life of 5 years.
d. depends on depth of water, rate of flow, organic content, etc.

FIGURE 1-3
ESTIMATED MOVEMENT OF PCBs THROUGH THE ENVIRONMENT

PCB isomers, whereas hydrospher [illegible] ies appear to be enriched in the higher-chlorinated compound [illegible] latter effect is magnified by the preferential biodegrada [illegible] microorganisms of tetrachloro and lower isomers. It is therefore difficult to ascertain which Aroclor was originally responsible for any given instance of pollution.

Although the possibility of accidental release to the environment will continue to pose a threat as long as PCBs remain in use, the implementation of available control technology can minimize loss during production, transport, storage, incorporation into products and disposal. The use of closed or sealed systems is suggested at production and industrial facilities wherever possible and also during ship loading, unloading, storage and any transfer operations. Appropriate materials and containers for all procedures involving handling of PCBs are described in publications by Monsanto, the Institute of Electrical and Electronics Engineers, and the American National Standards Institute. Release to the atmosphere may be controlled by a variety of techniques. Monsanto, for instance, employs Brink Mist Eliminators in all vapor lines to condense and collect vapors in the plant. In addition, all air from the ventilation system is passed through a high temperature incinerator (2000°F) which completely destroys the PCBs. Calgon has developed an activated carbon adsorption system known as "VentSorb" which may be hooked up to the vent of a storage tank or other point source. It is possible that this unit may be adapted to a ventilation system and adsorb PCBs from the air stream.

The recommended method for disposal of waste PCBs and PCB-containing products is through high temperature incineration (>2000°F). Many disposal services which properly incinerate all suitable PCB-containing waste materials are available to user industries for a fee. General Electric has recently installed a special incinerator of its own exclusively for liquid wastes (askarel). This incinerator operates under a different principal requiring lower temperatures (1200° to 1800°F) and 50 to 100 percent excess oxygen and results in virtually zero emission of PCBs to the atmosphere. Since municipal incinerators probably do not operate under appropriate conditions for destruction of PCBs and since they handle the unlabelled PCB-containing refuse dispersed in the environment, these incinerators should be fitted with scrubbers which can remove PCB vapors and PCB-containing particulates prior to venting. A variety of such scrubbers is available.

Loss to the atmosphere can be reduced to acceptable levels only if loss to the hydrosphere and lithosphere are controlled as well. The primary pathway for loss to the hydrosphere is contamination of sewers and subsequently of wastewater effluent. Ideally, all sewer systems that may contain PCBs should be isolated from a plant's effluent stream. Contaminated waste water may then be passed through such devices as a carbon adsorption or solvent extraction system. Calgon is planning a service called the Calgon Adsorption Service which will install an activated carbon unit, monitor effluents, prepare a monthly report, and guarantee a discharge in the parts-per-trillion range. Unfortunately, no methodology is presently available which can guarantee zero discharge to the hydrosphere from a point source effluent. This is an area where more research is essential.

The major loss to the lithosphere results from leaks and spills. Prompt clean up, using appropriate absorptive materials is recommended. Suitable materials include the bags, blankets, and boxes marketed by Gedcor and produced from Dow "imbiber beads." These soak up the askarel and allow it to be transported safely for proper disposal. Leakage from malfunctioning transformers must also be contained, followed by proper clean-up procedures. Placement of imbiber blankets in the containment areas under transformers is, for example, standard procedure at Dow Chemical Company.

Adequate methodology is available for those industries wishing to control the release of PCBs to the environment. There is, however, a need for a single comprehensive publication describing this methodology along with safeguards for worker protection, handling and shipping procedures, techniques for clean-up of spills and proper disposal practices. The EPA Oil and Hazardous Materials Spills Research Branch in Edison, New Jersey, is now in the process of preparing such a manual. A legal basis for compliance with any recommendations may, however, be necessary in order to ensure cooperation.

Controls and emission standards for PCBs are necessary because PCBs are highly toxic to most life forms, including man. Although human exposure to PCBs is mainly through the diet, PCBs will be inhaled whenever they exist in the atmosphere. The compounds are readily absorbed by both routes and tend to accumulate in body tissues. PCBs are stored preferentially in those tissues having a high lipid content and it is estimated that 41 to 45 percent of the general population have PCB levels of 1 ppm or more in their adipose tissue. Ease of metabolism seems to decrease with increasing chlorine content. The lower-chlorinated isomers undergo hydroxylation followed by conjugation with glucuronic acid and excretion in the urine. The more highly chlorinated isomers remain in the various tissues of the body.

The major site of toxic action for PCBs is the liver. Effects include increase in liver weight, induction of microsomal enzymes (which play a role in metabolizing foreign substances), and structural changes such as increases in lipid droplets within the cytoplasm and in lysozyme content. Concentrations of Aroclor 1254 as low as 0.15 ppm in the air were sufficient to produce noticeable changes in rat liver. Ambient levels of PCBs in urban areas such as Providence, Rhode Island, are approximately 1.6×10^5 times lower than this; however, the limits set for industrial exposure by the American Conference of Governmental Industrial Hygienists are 0.05 ppm, or only three times lower. It is obvious that more studies must be initiated which will elucidate the effects of low concentrations of PCBs on the human liver. It is suggested that the present permissible exposure levels be re-evaluated.

Dermal effects were among the earliest recognized signs of PCB toxicity in industrial workers handling PCBs or PCB-containing products.

An outbreak of PCB poisoning in Japan also resulted in widespread skin disease. Symptoms included acneform eruptions, increased pigmentation of the skin, lips, gums, nails, and mucous membrane of the mouth, itching of the skin and stiffening of the soles of the feet and palms of the hands. Concentrations as low as 300 ppm in the entire diet were sufficient to produce these symptoms in sub-human primates within three months. Concentrations ingested with milk fat (28 ppm) and fish (35 ppm) are only 10 times less than this. (Note these values exceed current Food and Drug Administration [FDA] temporary tolerances.) Gastrointestinal symptoms, including nausea and vomiting as well as certain cytological changes indicative of eventual neoplastic transformation, were also observed.

Other effects observed during the poisoning episode in Japan included changes in blood composition and bone marrow histology and sensory nerve involvement symptomized by numbness, pain, dulled sensitivity to touch, and absence of reflexes. Teratogenicity was also observed and took the form of abnormally early appearance of teeth, calcification of the skull, wide fontanelles and abnormal protrusion of the eyeballs. No direct instance of carcinogenesis in humans attributable to PCBs exists, although the aforementioned possibly pre-cancerous stomach lesions are suggestive of a carcinogenic potential for these compounds. Hepatocellular carcinomas have been produced in mice exposed to 300 ppm Aroclor 1254 in the diet for 11 months.

PCBs have also been found to be toxic to fish and birds and are most likely toxic to mammalian wildlife. Reduced egg production, hatching and survival of offspring are among the major effects observed in non-mammalian organisms.

II. PHYSICAL AND CHEMICAL PROPERTIES

A. SUMMARY

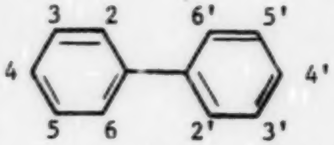
Polychlorinated biphenyls (PCBs) are substituted derivatives of the compound biphenyl in which from one to ten of the hydrogen atoms have been replaced by chlorine. Synthesized commercially as mixtures of isomers, PCBs are produced in the United States only by the Monsanto Company, which markets them under the trade name Aroclor. While individual chlorobiphenyls are solids at room temperature, the commercial mixtures are predominantly mobile oils. Their thermal stability, non-flammability and excellent electrical insulating properties give a wide variety of applications. Since PCBs are extremely hydrophobic, they are soluble in most of the common organic solvents and are only very slightly soluble in water. Aqueous solubility of both individual isomers and mixtures in general decreases with increasing chlorine content. Vapor pressures are also low and parallel solubility, with the preparations containing a higher percentage of less-chlorinated isomers being most volatile.

PCBs tend to adhere to smooth surfaces. This property, along with their lipophilicity, is responsible for their presence in the environment adsorbed to sediment and transported via airborne particulates.

Polychlorinated biphenyls are resistant to oxidizing agents, acids, bases, and a variety of other chemicals. They are, however, susceptible to photochemical degradation at wavelengths equivalent to those of ultraviolet (U.V.) light (~300 nanometers, or nm). The major photochemical reaction is reductive dechlorination with ortho chlorines preferentially replaced. In hydroxylic solvents or aqueous suspension, replacement by alkoxy or hydroxy groups also occurs. Evidence suggests that, under photochemical conditions leading to the formation of oxygenated products, toxic chlorodibenzofurans may be formed from 2-chloro biphenyls.

B. GENERAL DESCRIPTION AND PHYSICAL PROPERTIES

Polychlorinated biphenyls are substituted derivatives of the compound biphenyl (I) in which anywhere from one to ten of the hydrogen atoms have been replaced by chlorine.



I

Although 209 chlorinated biphenyl isomers are theoretically possible, from both a statistical and mechanistic standpoint it is unlikely that all are formed in the technical chlorination process. Certain isomers, such as 2,3,4,5,6-pentachlorobiphenyl for instance, where one ring is fully chlorinated and the other not at all, would be highly disfavored (Hutzinger *et al*., 1974).

PCBs are prepared industrially by the chlorination of biphenyl with anhydrous chlorine using iron filings or ferric chloride as catalyst. The resulting product is a complicated mixture of isomers with the highest proportion of compounds corresponding in composition to the average chlorine content. Domestic PCBs, produced by the Monsanto Company, are marketed under the trade name Aroclor. Each Aroclor mixture is characterized by a four digit number in which the first two digits, 12, indicate chlorinated biphenyl and the last two give the weight (w/w) percent of chlorine in the mixture. An exception to this nomenclature is a recent product, Aroclor 1016, which contains 41 percent chlorine by weight but reduced quantities of the penta-, hexa-, and heptachlorobiphenyl isomers. Typical percent compositions of some Aroclor mixtures are presented in Table 2.1. The most common substitution patterns for the chlorobiphenyls found in PCB preparations are presented in Figure 2.1. Due to the ready availability of the Aroclor mixtures and their wide use as such, most determinations of physical properties are performed on Aroclor as opposed to individual PCB isomers. Some important physical properties of the various Aroclor mixtures are presented in Table 2.2. One major difference between the commercial mixtures and the individual isomers is their solidification points. Most individual chlorobiphenyls are solids at room temperature, whereas commercial mixtures are mobile oils (Aroclor 1221, 1232, 1242, and 1248), viscous liquids (Aroclor 1254), or sticky resins (Aroclor 1260 and 1262) due to the mutual depression of melting points by the component isomers (Hutzinger et al., 1974).

The physical characteristics which render PCB mixtures useful are their thermal stability, non-flammability, and excellent dielectric

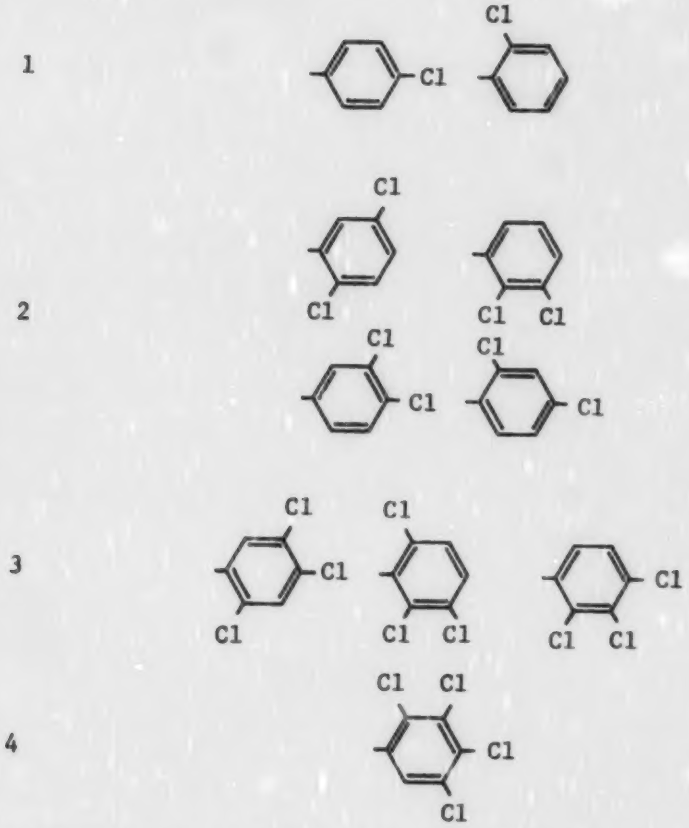
TABLE 2.1 TYPICAL PERCENT COMPOSITION OF SOME POLYCHLORINATED BIPHENYL PRODUCTS*

HOMOLOG # Cl/BIPHENYL	AROCLOR 1221	AROCLOR 1016	AROCLOR 1242	AROCLOR 1254
0	11	<0.1	<0.1	<0.1
1	51	1	1	<0.1
2	32	20	16	<0.5
3	4	57	49	1
4	2	21	25	21
5	<0.5	1	8	48
6	ND	<0.1	1	23
7	ND	ND	<0.1	6
8	ND	ND	ND	ND

*Percent (w/w) by GC/MS (Gas Chromatography/Mass Spectrometry).

ND = none detected, <0.01%

Source: Hutzinger, O., S. Safe, and V. Zitko, "The Chemistry of PCBs," CRC Press, Cleveland, Ohio, 1974.


1
Cl
Cl
2
Cl
Cl
Cl Cl
Cl
Cl
Cl
Cl
3
Cl
Cl
Cl
Cl
Cl Cl
Cl
Cl Cl
4
Cl Cl
Cl
Cl

* Only one phenyl-ring is shown. The most abundant tetrachlorobiphenyls, for example, are those from the dichlorophenyl-moieties shown. One di- and one trichlorophenyl- would give most abundant penta-chlorobiphenyl etc.

Source: Hutzinger, O., S. Safe, and V. Zitko, "The Chemistry of PCBs," CRC Press, Cleveland, Ohio, 1974.

FIGURE 2.1

THE MOST COMMON SUBSTITUTION PATTERNS FOR THE CHLOROBIPHENYLS FOUND IN PCB PREPARATIONS*

Table 2.2 PHYSICAL PROPERTIFS OF VARIOUS AROCLOR MIXTURES

	1221	1232	1242	1248	1254	1260	1262	1268	1016
Average Molecular weight	192	221	261	288	327	372	389	453	NR
% Cl	20.5-21.5	31.5-32.5	42	48	54	60	61.5-62.5	68	41
Average number of Cl/moleclue	1.15	2.04	3.10	3.90	4.96	6.30	6.80	8.70	NR
Appearance	clear mobile oil	clear mobile oil	clear mobile oil	clear mobile oil	light yellow viscous fluid	light yellow soft sticky resin	light yellow sticky viscous resin	white to off white powder	clear mobile oil
Specific gravity	1.182-1.192 (25°C/ 15.5°C)	1.270-1.280 (20°C/ 15.5°C)	1.381-1.392 (25°C/ 15.5°C)	1.405-1.405 (65°C/ 15.5°C)	1.495-1.505 (65°C/ 15.5°C)	1.555-1.566 (90°C/ 15.5°C)	1.572-1.583 (90°C/ 15.5°C)	1.804-1.811 (25°C/ 25°C)	1.362-1.372 (25°C/ 15.5°C)
Density (lbs/gal, 25°C)	9.85	10.55	11.50	12.04	12.82	13.50	13.72	15.09	NR
Distillation range °C, corrected (ASTM D-20, mod)	275-320	290-325	325-366	340-375	365-390	385-420	390-425	435-450	323-356
Evaporation loss, % 100°C, 6 hours 163°C, 5 hours (ASTM D-6, mod)	 1.0-1.5 --b	 1.0-1.5 --	 0-0.4 3.0-3.6	 0-0.3 3.0-4.0	 0-0.2 1.1-1.3	 0-0.1 0.5-0.8	 0-0.1 0.5-0.6	 0-0.06 0.1-0.2	 NR NR
Vaporization rate ($g/cm^2/hr$)* at 100°C (surface area = 12.28 cm^2)	$1.74x10^{-3}$	$8.74x10^{-4}$	$3.38x10^{-4}$	$1.52x10^{-4}$	$5.3x10^{-5}$	$9x10^{-6}$	$1.3x10^{-5}$	NR	NR

*$g/cm^2/hr$ = gram square centimeter/hour

TABLE 2.2 (Continued)

	1221	1232	1242	1248	1254	1260	1262	1268	1016
Flash point (Cleveland open cup) °C	141-150	152-154	176-180	193-196	none to boiling point	none to boiling point	none to boiling point	none to boiling point	170
Fire point (Cleveland open cup) °C	176	238	none to boiling point	none to boiling point	none to boiling point	none to boiling point	none to boiling point	none to boiling point	none to boiling point
Refractive index, N_D^{20} 20°C	1.617-1.618	1.620-1.622	1.627-1.629	1.630-1.631	1.639-1.641	1.647-1.649	1.650-1.652	---	1.622-1.624 (@25°C)
Viscosity, seconds Saybolt universal (ASTM D-83) 37.8°C	38-41	44-51	82-92	185-240	1800-2500	---	600-850 (at 71°C)	---	71-81
54.4°C	35-37	39-41	49-56	73-80	260-340	3200-4500		---	NR
98.9°C	30-31	31-32	34-35	36-37	44-48	72-78	86-100	---	NR

--- = not applicable
NR = not reported
ASTM = American Society for Testing Materials.

Source: Modified from Hutzinger, O., S. Safe, and V. Zitko, "The Chemistry of PCBs," CRC Press, Cleveland, Ohio, 1974.

(electrical insulating) properties. The flash and fire points are included in Table 2.2; the electrical properties of some Aroclors are presented in Table 2.3.

The most important physical properties of PCBs from an environmental point of view are solubility and vapor pressure. Like the chlorinated hydrocarbon insecticides, PCBs are extremely hydrophobic and would therefore be expected to occur in lipid phases such as the organic films sometimes found on the surface of natural waters (Crosby and Moilanen, 1973). The oils and resins are readily soluble in most of the common organic solvents whereas the crystalline isomers and mixtures such as Aroclor 1268 are less soluble (Hubbard, 1964). All are insoluble in glycerol and the glycols (Hubbard, 1964; Hutzinger _et al._, 1974). The solubilities of 21 PCB isomers in water as determined by Wallnöfer _et al_. (1973) are presented in Table 2.4. More recent determinations (Haque and Schmedding, 1975) on four of these isomers and one additional isomer are also given. It can be seen from this table that the water solubilities of all PCB isomers are low and, in general, decrease with increasing chlorine content. The values reported by Haque and Schmedding are somewhat lower than those of Wallnöfer _et al_. These authors attribute this discrepancy to failure on the part of the earlier workers to allow sufficient time for equilibrium to take place (Wallnöfer _et al_. allowed only 2 hours, whereas complete equilibrium, according to Haque and Schmedding, requires at least one month). Thus, aggregates of PCBs which would have made their way to

TABLE 2.3 ELECTRICAL PROPERTIES OF SOME AROCLORS

AROCLOR	DIELECTRIC CONSTANT AT 1000 CYCLES[a]		VOLUME RESISTIVITY,[b] 8 cm AT 100°C 500 V, dc	DIELECTRIC STRENGTH,[c] kV	POWER FACTOR,[a] 100°C, 1000 CYCLES, %
	25°C	100°C			
1232	5.7	4.6			
1242	5.8	4.9	above 500×10^9	>35	<0.1
1248	5.6	4.6	above 500×10^9	>35	<0.1
1254	5.0	4.3	above 500×10^9	>35	<0.1
1260	4.3	3.7	above 500×10^9	>35	<0.1
1268	2.5				
1016[g]	NR	4.9[d]	above 500×10^9[e]	>35	NR[f]

[a] ASTM D-150-47T

[b] ASTM D-257-46

[c] ASTM D-149-44

[d] 60 cycles

[e] Inferred from measurement at 500 VDC, 100°C, 0.1" gap

[f] Same as for 1242 at 60 hz

[g] Values for Aroclor 1016 obtained from Monsanto specification sheet

Source: Hutzinger, O., S. Safe, and V. Zitko,
"The Chemistry of PCBs." CRC Press, Cleveland, Ohio, 1974.

TABLE 2.4 SOLUBILITY OF CHLOROBIPHENYLS IN WATER

COMPOUND	SOLUBILITY (ppm) (Wollnöfer *et al.*, 1973)	(Haque and Schmedding, 1975)
Monochlorobiphenyls		
2-	5.9	
3-	3.5	
4-	1.19	
Dichlorobiphenyls		
2,4-	1.40	
2,2'-	1.50	
2,4'-	1.88	0.637 ± 0.004
4,4'-	0.08	
Trichlorobiphenyls		
2,4,4'-	0.085	
2',3,4-	0.078	
2,2',5-	-	0.248 ± 0.004
Tetrachlorobiphenyls		
2,2',5,5'-	0.046	0.0265 ± 0.0008
2,2',3,3'-	0.034	
2,2',3,5'-	0.170	
2,2',4,4'-	0.068	
2,3',4,4'-	0.058	
2,3',4',5-	0.041	
3,3',4,4'-	0.175	
Pentachlorobiphenyls		
2,2',3,4,5'-	0.022	
2,2',4,5,5'-	0.031	0.0103 ± 0.0002
Hexachlorobiphenyl		
2,2',4,4',5,5'-	0.0088	0.000953 ± 0.00001
Octachlorobiphenyl		
2,2',3,3',4,4',5,5'-	0.0070	
Decachlorobiphenyl	0.015	

Sources: Haque, R. and Schmedding, D., "A Method of Measuring the Water Solubility of Hydrophobic Chemicals: Solubility of Five Polychlorinated Biphenyls." Bulletin of Env. Contamin. and Tox. 14, 13-18 (1975).

Wollnöfer, P.R., Koniger, M., and Hutzinger, O., "The Solubilities of Twenty-One Chlorobiphenyls in Water", Analab Res. Notes 13, 14-16 (1973).

the surface, may have been sampled along with dissolved material. In addition, it is suggested that the water in the earlier study may have been contaminated with organic impurities, falsely increasing the effective concentration of dissolved PCB. The solubilities of some Aroclor mixtures are presented in Table 2.5.

Another determination of the solubility of Aroclor 1254 in water (Haque et al., 1974) revealed a value of 56 ppb at room temperature, in good agreement with the previous study. Once again, those mixtures richer in the less-chlorinated species exhibit a greater degree of solubility. Table 2.6 summarizes the relative gas chromatography (GC) peak heights of a saturated aqueous solution of Aroclor 1254 (Hutzinger et al., 1974). It can be seen that the first few peaks, which, in general, correspond to the lesser-chlorinated isomers, are significantly higher than the equivalent peaks in the standard Aroclor 1254. Determinations of the solubilities of PCBs in water are complicated by the fact that these compounds tend to adsorb to smooth surfaces such as glass, metal, varnished or lacquered surfaces, and plastic (Hubbard, 1964; Hutzinger et al., 1974). This tendency, along with their lipophilicity, is responsible for the ultimate accumulation of PCBs in sediment and their transport through the environment via airborne particulates.

The vapor pressure of several Aroclor preparations determined over a wide range of temperatures is presented in Figure 2.2 and the actual values at 37.8°C are listed in Table 2.7. Vapor pressures parallel

TABLE 2.5 THE SOLUBILITIES OF AROCLOR MIXTURES, 20°C

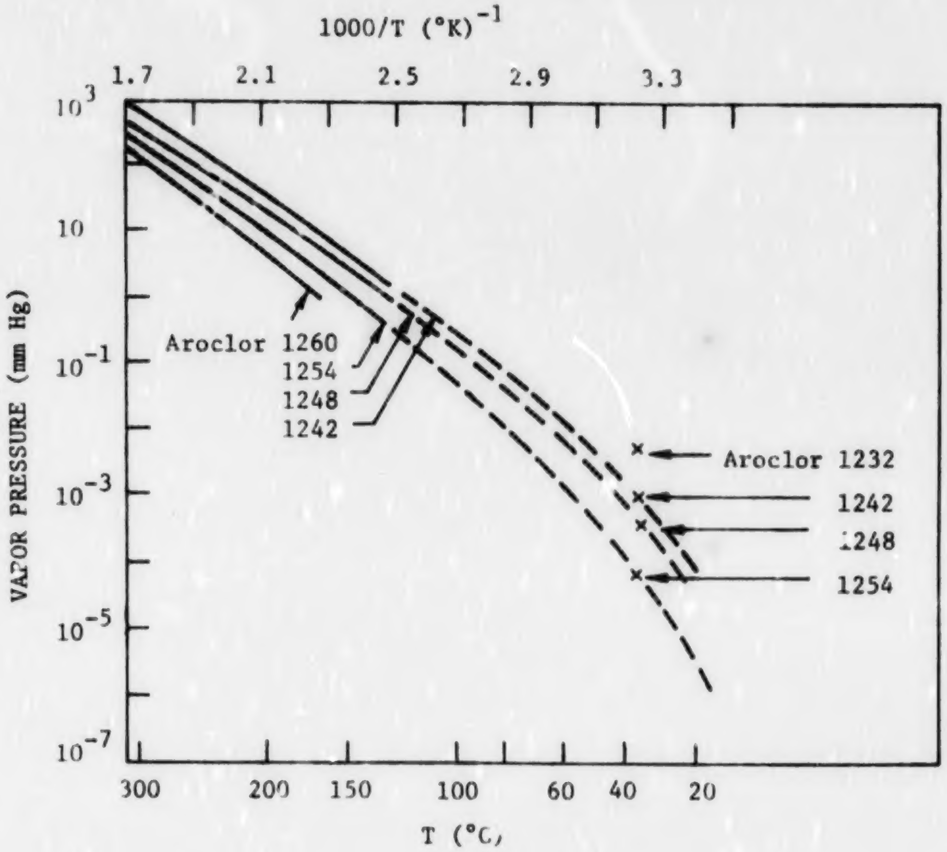
AROCLOR	SOLUBILITY (ppb)
1242	200
1248	100
1254	40
1260	25

Source: Panel on Hazardous Trace Substances, "Polychlorinated Biphenyls -- Environmental Impact." Environmental Research 5: 249 (1972).

TABLE 2.6 RELATIVE GAS CHROMATOGRAPH PEAK HEIGHTS (PEAK 5 - 100) IN SATURATED AQUEOUS SOLUTIONS OF AROCLOR 1254

PEAK NO.	SATURATED AQUEOUS SOLUTION (26°C)	SATURATED AQUEOUS SOLUTION (4°C)	AROCLOR 1254 STANDARD
1	172	144	35
2	91	72	16
3	47	41	30
4	14	9	1
5	100	100	100
6	33	28	23
7	57	59	55
8	5	5	10
9	21	24	25
10	8	13	31
11	4	4	6
12	11	24	50
13	6	10	11

Source: Hutzinger, O., S. Safe, and V. Zitko, "The Chemistry of PCBs." CRC Press, Cleveland, Ohio, 1964.



Source: Hutzinger, O., S. Safe, and V. Zitko, "The Chemistry of PCBs," CRC Press, Cleveland, Ohio, 1974.

FIGURE 2.2
VAPOR PRESSURES OF DIFFERENT AROCLOR PREPARATIONS

TABLE 2.7 APPROXIMATE VAPOR PRESSURE OF AROCLOR PREPARATIONS AT 37.8°C

Aroclor 1232	0.005 mm. Hg
Aroclor 1242	0.001 mm. Hg
Aroclor 1248	0.00037 mm. Hg
Aroclor 1254	0.00006 mm. Hg

Source: Monsanto, "Aroclor Plasticizers," Monsanto Technical Bulletin O/PL-306A, undated.

solubility in that the preparations containing a higher percentage of the less-chlorinated isomers are more volatile. When 1 mg of Aroclor 1254 is heated with 300 ml of water (conditions of codistillation), the earlier GC peaks corresponding to the less-chlorinated isomers are seen to decrease more rapidly than those peaks representing the more highly chlorinated compounds (Table 2.8). This difference is, however, much smaller when the same amount of Aroclor is heated in the absence of water (Hutzinger et al., 1974). Other data bearing on the volatility of Aroclors, such as the percent loss through evaporation at 100°C (6 hours) and 163°C (5 hours) and the vaporization rate in grams/ square centimeter/hour ($g/cm^2/hr$) at 100°C for a surface area of 12.28 cm^2, are given in Table 2.2.

Studies relating the pertinent physical properties of solubility and volatility to occurrence (either potential or actual) in the environment will be discussed in the appropriate subsection of Section IV.

C. SPECIFIC CHEMICAL PROPERTIES

Polychlorinated biphenyls are generally considered to be inert compounds, which renders them extremely useful in a wide variety of applications. Along with the previously mentioned properties of thermal stability and non-flammability, PCBs also exhibit marked resistance to oxidizing agents, acids, bases, and other chemicals. Under vigorous conditions, however, certain reactions do take place.

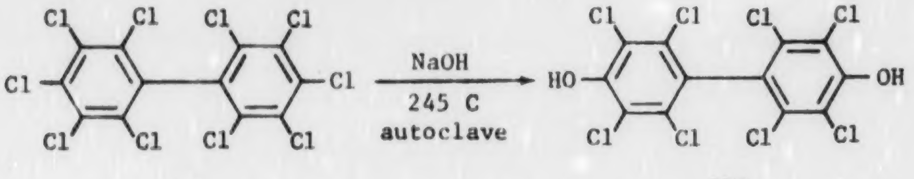
Treatment of decachlorobiphenyl (II) with aqueous alkali in an autoclave at high temperatures results in the formation of octachloro-

TABLE 2.8 PERCENT LOSS IN AREA OF SEVEN CHROMATOGRAPH PEAKS OF AROCLOR AROCLOR 1254 AFTER HEATING ON A STEAM BATH

	% PEAK REMAINING AFTER HEATING		
	WITH WATER		WITHOUT WATER
AROCLOR 1254 PEAK	25 MIN	60 MIN	10 MIN
1	34	17	13
2	59	26	15
3	78	27	20
4	60	46	20
5	86	49	27
6	100	85	28
7	100	67	16

Source: Hutzinger, O., S. Safe, and V. Zitko, "The Chemistry of PCBs." CRC Press, Cleveland, Ohio, 1974.

4,4'-biphenylol (III) (Hutzinger _et al._, 1974). The 4,4'-methoxy derivatives are also formed under similar conditions using sodium methoxide or under milder conditions using sodium methoxide in pyridine. These nucleophilic displacement reactions occur preferentially at the para position, possibly due to the resonance stabilized intermediate that results from para attack.



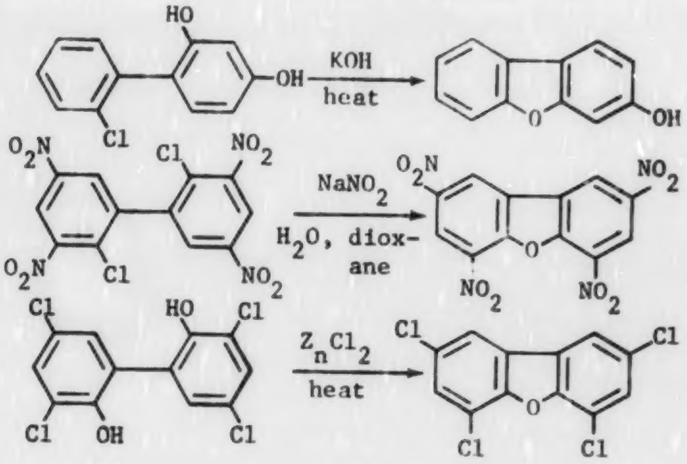
II III

Although a mixture of chromic anhydride and acetic acid is able to oxidize mono-, di-, and trichlorobiphenyls to the corresponding chlorobenzoic acids, the oxidation of PCB mixtures with averages of 5 or 7 chlorine atoms per molecule requires boiling nitric acid. Potassium permanganate, chromic acid, and nitric acid treatment under milder conditions proved ineffective.

Reductive dechlorination of decachlorobiphenyl to yield nona- and octa- chlorobiphenyls in which the 4 and/or 4' chlorine is replaced can be effected by use of lithium aluminum hydride, butyl lithium and water, or the Grignard reagent and water.

Nitration is another possible reaction which occurs in both the highly chlorinated and lesser chlorinated PCB isomers. With the latter, the extent of nitration may be controlled by varying the reaction conditions.

The last reaction to be mentioned is the cyclization of 2- and 2,2'-substituted biphenyls to yield highly toxic dibenzofuran derivatives. The close proximity of the 2 and 2' substituents facilitates cyclization under a variety of conditions. Some examples are shown below.


HO
OH
KOH
heat
Cl
OH
O
O_2N
Cl
Cl
NO_2
$NaNO_2$
H_2O, dioxane
O_2N
NO_2
O_2N
Cl
NO_2
O
NO_2
NO_2
Cl
HO
Cl
$ZnCl_2$
heat
Cl
Cl
Cl
OH
Cl
O
Cl
Cl

"In view of the remarkable chemical stability of polychlorinated biphenyls, environmental breakdown initiated by the photochemically active part of the solar spectrum is of particular interest" (Hutzinger et al., 1974).

Photochemical degradation is probably the sole pathway (except for biodegradation) for breakdown of these compounds in the environment, and several studies dealing with the irradiation of pure chlorobiphenyl isomers at wavelengths above 290 nm (the lowest wavelength of the radiation generally received from the sun at the earth's surface) have been reported. Irradiation of PCBs in the vapor phase or in the solid state as a thin film adsorbed onto a glass surface has been attempted but the results for the most part are inconclusive. Irradiation of orthochlorobiphenyl at 300-310 nm under normal lower atmospheric conditions resulted in the formation of quantitative amounts of HCl along with unidentified aldehydes and phenolic compounds. One probable product was orthohydroxy biphenyl (Arnts, 1975). The only truly definitive experiments in which products have been identified are those conducted in solution. Due to the low aqueous solubility of PCBs, these experiments have been carried out in organic solvents. The studies are, however, environmentally significant since organic hydrogen donors are abundant in nature, existing in the form of oil films, cuticular waxes, the surface microlayer of the ocean, and so forth. It is in these "mixed" aqueous and organic compartments that PCBs are most likely to reside. In general, reductive dechlorination is the main initial photochemical reaction of PCBs in organic solvents (Hutzinger et al., 1974; Ruzo et al., 1974). The rate of the reaction is more rapid in polar, hydroxylic solvents (alcohols) than in non-polar solvents and, in the former case, substitution of chlorine by an alkoxy group is also observed. In a recent study, Ruzo et al. (1974) selected six highly toxic tetrachlorobiphenyls and determined the products formed following irradiation at 300 nm for 10 to 15 hours in both hexane and methanol. The results are summarized in Table 2.9. Between 90 and 95 percent of the starting material reacted. Trichlorobiphenyls and di-

TABLE 2.9 PHOTO PRODUCTS OF IRRADIATION OF SIX TETRACHLOROBIPHENYLS IN HEXANE AND METHANOL

POLYCHLORINATED BIPHENYL	DECHLORINATED PRODUCTS[a]	METHOXYLATED PRODUCTS[b]
2,2',5,5'-Tetrachlorobiphenyl	2,3',5-Trichlorobiphenyl 3,3'-Dichlorobiphenyl 3-Chlorobiphenyl	Trichloromethoxybiphenyl Dichlorodimethoxybiphenyl
2,2',4,4'-Tetrachlorobiphenyl	2,4,4'-Trichlorobiphenyl 4,4'-Dichlorobiphenyl 4-Chlorobiphenyl	Trichloromethoxybiphenyl Dichlorodimethoxybiphenyl
2,2',3,3'-Tetrachlorobiphenyl	2,3,3'-Trichlorobiphenyl 3,3'-Dichlorobiphenyl	Trichloromethoxybiphenyl Dichlorodimethoxybiphenyl
3,3',4,4'-Tetrachlorobiphenyl	3,4,4'-Trichlorobiphenyl 4,4'-Dichlorobiphenyl	Trichloromethoxybiphenyl
3,3',5,5'-Tetrachlorobiphenyl	3,3',5-Trichlorobiphenyl	
2,2',6,6'-Tetrachlorobiphenyl	2,2',6-Trichlorobiphenyl 2,2'-Dichlorobiphenyl	Trichloromethoxybiphenyl

[a] formed in both hexane and methanol

[b] formed in methanol only

Source: Ruzo, L.O., M.J. Zabils, and R.D. Schuetz, "Photochemistry of Bioactive Compounds: Photo products and Kinetics of Polychlorinated Biphenyls," J. Agricul. & Food Chem. 22, 199-202 (1974).

chlorobiphenyls were the main reaction products in both solvents, with monochlorobiphenyls constituting less than 1 percent of the total product formation after 10 hours. In methanol, the amount of methoxylated products (of which the primary components were trichloromethoxy biphenyls) did not exceed 5 percent of total product formation. Methanol substitution took place at the same site at which chlorine was lost. Each tetrachlorobiphenyl that was irradiated containing chlorines in the ortho position yielded products arising from the loss of these, while those compounds containing only meta- and para-chlorines lost the meta-chlorines preferentially. This pattern was also observed in the formation of the secondary products, the dichlorobiphenyls in which ortho- and meta- but not para-chlorines were lost. The formation of monochlorobiphenyls in yields of less than 1 percent or not at all was most likely due to the failure of the dichlorobiphenyls to absorb sufficiently at the wavelengths employed. It is suggested that the dechlorination reactions are free radical in nature whereas the methoxylation reactions probably occur via nucleophilic attack by methanol followed by elimination of HCl. Of particular environmental interest is the fact that the reaction rates for dechlorination were found to increase considerably when solutions were degassed prior to irradiation, that is, when oxygen was removed from the system. The postulated excited state for the reaction is known as a "triplet." Oxygen is known to act as a triplet quencher by accepting excess electronic energy from excited molecules before any chemical change occurs. Thus, greater photochemical decomposition may be expected to occur under anaerobic conditions.

Because of the toxicity of chlorinated dibenzofurans, the possibility of their photochemical formation from PCBs must be considered. Hutzinger et al. (1973) have speculated that chlorodibenzofurans may be formed from chlorobiphenyls under photochemical conditions leading to the formation of oxygenated products--the formation of a chlorinated 2-biphenylol constituting a necessary intermediate. Although formation of polychlorinated 2-biphenylols has not been reported, Crosby et al. (1973) found that polychlorinated phenols formed chlorinated catechols and resorcinols following irradiation in aqueous media at wavelengths equivalent to sunlight. Displacement of the chlorine ortho to the oxygen predominated. Irradiation experiments with five pure 2-chlorinated biphenyls (5 milligrams/liter [mg/l] aqueous suspensions) revealed traces of 2-chlorodibenzofuran, although only the 2,5-dichloro- and 2,5,2',5'-tetrachlorobiphenyls provided identifiable amounts (a roughly steady 0.2 percent yield during a 7-day irradiation). Hutzinger et al. (1973) reported that preliminary studies suggest the formation of chlorodibenzofurans from 2,4,6,2',4',6'-hexachlorobiphenyl when irradiation takes place in methanol. Since chlorodibenzofurans are themselves photolabile, it seems unlikely that accumulation of these compounds formed from chlorobiphenyls by photochemical reaction in the environment will occur. Nevertheless, due to their toxicity, even their transient existence becomes important.

III. METHODS FOR SAMPLING AND ANALYSIS OF POLYCHLORINATED BIPHENYLS IN THE ATMOSPHERE

A. SUMMARY

Methods of atmospheric sampling for PCBs generally fall into one of three categories: liquid absorption systems, liquid phases on solid supports, and solid adsorbents. Liquid absorption systems, while popular, are suitable only when high concentrations of PCBs are expected. Air flow rates are limited in these systems, and a sample volume insufficient for detection of low-level PCB contamination is obtained. Liquid phases on solid supports usually involve use of some type of oil. Difficulties in removal of the oil from the sample, resulting in subsequent interference with analysis, is one major drawback to this type of system. The third type of methodology for atmospheric sampling employs a solid adsorbent. One promising material is polyurethane foam. A high flow rate is achieved and no interfering oils are necessary. Furthermore, the system is relatively selective for PCBs.

Following extraction of the PCBs from the sampling medium, removal of interfering compounds may be achieved by column chromatography. Silicic acid columns separate PCBs from DDT and other pesticides. Alumina removes additional electron capturing interferences. DDT may also be removed by saponification followed by extraction with sulfuric acid.

The most sensitive analytical procedure for PCBs is electron capture gas chromatography. Qualitative verification may be achieved by use of perchlorination or thin layer techniques. Mass spectrometry, when used in conjunction with gas chromatography, provides unequivocal confirmation of the presence of PCB residues and is the best procedure for characterizing the molecular composition of the observed residues.

B. INTRODUCTION

An assessment of the hazards presented by polychlorinated biphenyls in the atmosphere can only be as accurate as the methods employed for their sampling, detection, and quantitation. Although sophisticated analytical techniques for PCBs are available, the difficulties inherent in atmospheric sampling continue to create a significant obstacle to the establishment of an intensive, wide-range monitoring program. The low concentrations of PCBs expected in the ambient atmosphere far removed from their points of origin require that a large volume of air be sampled. On the other hand, practical considerations require that sampling must be completed within a reasonable length of time. Furthermore, vapor phase PCBs, as well as those adsorbed to particulates, must be trapped efficiently since both forms may contribute substantially to the total residues present.

In general, sampling of particulate-bound PCBs involves collection via filtration. Loss of PCBs from the filtered particulates may, however, ensue with volatilization to the air stream the most likely pathway. The rate of air flow through the sampling apparatus, the temperature, and the adsorptivity of the particulate surface are factors which determine the extent to which such loss occurs (Seiber et al., 1975). The volatility of the individual components would also affect their retention so that the PCB mixture finally subjected to analysis might be significantly different from that initially present in the atmosphere. Loss of small particulates through the filter itself poses another problem. Use of glass cloth or glass fiber filters capable of efficiently trapping particles as small as 0.1 micron in diameter have, however, minimized these losses (Seiber, et al., 1975).

Trapping of PCB vapors is usually performed by liquid extraction or absorption from the sampled air stream. Inaccuracies due to non-representative sampling, incomplete extraction, and revolatilization from the trapping medium frequently result.

In an effort to counteract these difficulties, attempts at determination of "sampling efficiency" have been undertaken. These attempts usually involve spiking the air with known amounts of PCBs as dusts and/or vapors and determining the overall recovery. However, difficulties in simulating natural sampling conditions render the usefulness of such results questionable (Seiber et al., 1975).

Additional problems associated with the sampling of PCBs in the atmosphere include: chemical degradation of the sampling medium; interference of the sampling medium (or its degradation products) in subsequent work up or analytical steps; difficulties with the quantitative removal of PCBs from the sampling medium; and simultaneous collection of interfering compounds (Seiber et al., 1975).

The methods for sampling and determination of PCBs in the atmosphere are generally similar to those used for the analysis of pesticide residues (Sherma, 1975). The entire operation involves the following overall steps:

a. Sampling of the atmosphere

b. Extraction of the PCBs from the sample

c. "Cleanup" of the extract to remove interfering substances

d. Qualitative and quantitative analysis

e. Confirmation by additional analytical techniques

While suitable sampling procedures for PCBs are still in the experimental stages, methods for extraction, cleanup, and analysis are fairly standardized.

C. SAMPLING FOR PCBs IN THE ATMOSPHERE

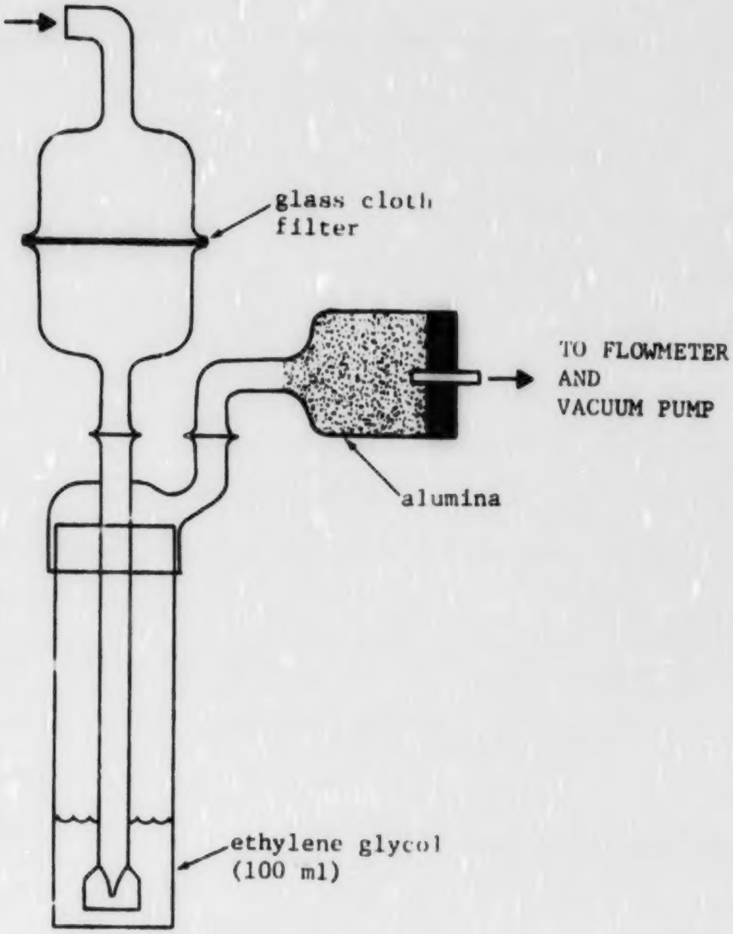
Presently, available sampling procedures generally fall under one of three headings: liquid absorption methods, liquid phases on solid supports, and solid adsorbents.

1. Liquid Absorption Methods

Liquid absorption methods usually involve the use of some type of impinger or fritted gas bubbler in conjunction with a vacuum pump. One popular procedure utilizes the Greenburg-Smith Impinger and consists of drawing air by vacuum pump through a trapping medium of ethylene glycol at a rate of from 10.3 to 30 liters per minute (U.S. Environmental Protection Agency, 1974; Kutz and Yang, 1975; Enos *et al.*, 1972; Enos, 1976). Hexylene glycol (Stanley *et* *al.*, 1971), hexane (Hochheiser, 1976), toluene (American National Standards Institute, 1974), and secondary butyl alcohol (American Industrial Hygiene Association, 1965) have also been used, although the first of these alternatives resulted in significantly greater interference in subsequent analytical steps (Seiber *et al.*, 1975). Immersion of the ethylene glycol impinger in an ice bath (Hochheiser, 1976) presumably inhibits vaporization losses. An ethylene glycol impinger system is presented in Figure 3.1. The alumina adsorption "backup" also shown in this diagram, may sometimes be employed, although use of a backup adsorbant often results in additional analytical interference (Seiber *et al.*, 1975).

The method has been found to work reasonably well with a variety of pesticides and has proven efficient for both vapors and dusts. In those cases where an alumina backup was employed, significant amounts of trapped chemicals were detected in all three sampler components (the impinger solution, the glass filter, and the adsorption backup). Levels as low as 0.1 ng/m^3 were detectable for many compounds (Seiber *et al.*, 1975).

This method is currently employed for PCBs by the Ecological Monitoring Branch of the U.S. Environmental Protection Agency (Kutz and Yang, 1975) and is advocated by the American National Standards Institute (ANSI) (1974); however, the efficiency for PCB collection has never been fully evaluated (Enos, 1976).


glass cloth filter
TO FLOWMETER AND VACUUM PUMP
alumina
ethylene glycol (100 ml)

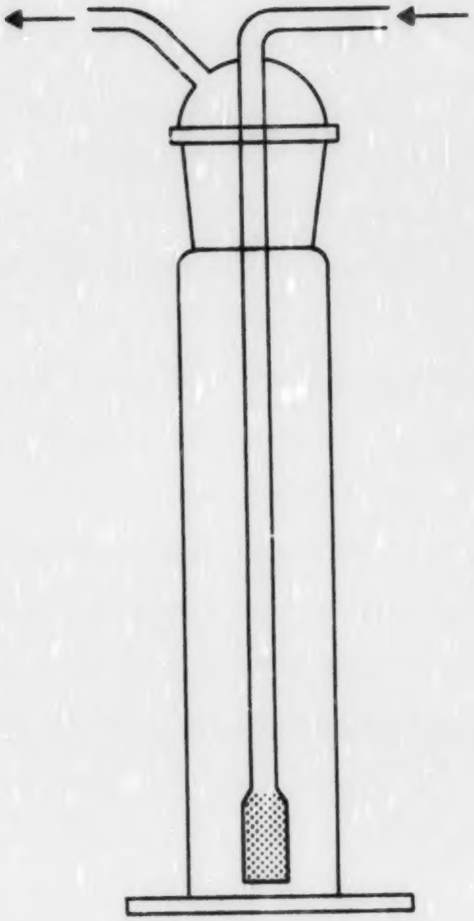
Source: Adapted from Seiber, J.N., J.E. Woodrow, T.M. Shafik, and H.P. Enos. 1975. "Determination of Pesticides and Their Transformation Products in Air," in Environmental Dynamics of Pesticides: 17-43. Plenum Press, New York and London.

Figure 3.1. FILTER, IMPINGER, AND ADSORPTION SAMPLING TRAIN

A typical fritted glass bubbler is shown in Figure 3.2. Both particulates and vapors are also trapped by these devices. Particulates adsorb to the fritted glass and the PCBs are extracted from the adsorbed particulates by the organic solvent in which the fritted glass is immersed. It is advisable to surge the solvent back and forth through the fritted glass several times before a sample is withdrawn for analysis (Hendrickson, 1968). The solvent most frequently used for PCB collection is toluene and the method is also recommended by ANSI (ANSI, 1974; Hochheiser, 1976).

As in the case of the ethylene glycol impinger, neither the capacity nor the efficiency of the fritted gas bubbler for removal of airborne PCBs has been experimentally evaluated. Therefore, to obtain measurable amounts of PCBs, it is best to minimize the sampling flow rate and maximize the sampling time period. When high flow rates must be employed, or when a larger air volume is required, it is recommended that several gas bubblers be used in tandem (ANSI, 1974).

Several limitations are inherent in liquid absorption systems. The most important of these is the difficulty of collecting a sufficient sampling volume. Air flows are limited to about 30 liters per minute, so that a 24-hour sampling period results in the collection of PCBs from a total of only 43 cu m of air (Kutz and Yang, 1975). While an increased sampling period is possible, losses from the impinger reportedly increase upon prolonged sampling and are greater with more volatile compounds (Seiber, 1975). Samples collected by EPA (U.S.



Source: Adapted from Hendrickson, E.R. 1968. "Air Sampling and Quantity Measurement," in Air Pollution II. Second Edition. Academic Press, New York and London.

Figure 3.2 A TYPICAL FRITTED-GLASS BUBBLER USED IN SAMPLING FOR GASES

Environmental Protection Agency, 1974) usually of 400 ml of ethylene glycol, representing the contents of four impingers of 100 ml each, two of which are operated simultaneously for 12 hours, and the other two for an additional 12 hours. The total air volume sampled is about 80 cu m (U.S. Environmental Protection Agency, 1974). An additional shortcoming of this method is that the equipment is very expensive and quite fragile. Finally, the system also traps numerous interfering pesticides, thus requiring additional cleanup steps which inevitable result in further loss of PCBs.

Liquid absorption methods appear most suitable for sampling at sites where relatively high concentrations are expected, such as near investment casting foundries, capacitor manufacturing plants, and low temperature incinerator stacks. Due to the absence of data relating to the efficiency and capacity of these systems, they may only be considered accurate for the measurement of relative PCB concentrations sampled under identical conditions. The methods are not appropriate for general ambient sampling (Enos, 1976).

2. Liquid Phases on Solid Supports

Liquid phases on solid supports fall into one of two categories. The first category includes those samplers designed as an alternative to liquid absorption systems. These samplers are used in conjunction with a vacuum pump and, due to the porosity of the solid support, allow a flow rate approximately 10 times that achieved by impinger style collectors. The second category includes those samplers designed for static air sampling. These samplers are suitable for comparison of contamination levels from one location to another, but do not permit the calculation of concentrations (Seiber et al., 1975). The variety of such collection systems used to date for PCBs and similar compounds (the organochlorine insecticides, for example) are summarized in Table 3.1.

Of the high volume samplers, the only types which have been specifically applied to PCBs are the silicone oil coated ceramic saddle system of Harvey and Steinhauer (1974) and the glycerine-florisil system of Wakimoto et al. (1974). In the former case, a 3.0 μm glass fiber filter was inserted in front of the coated saddles to trap particulates. It was expected that PCBs in the vapor and aerosol phase would easily pass through the filter and be trapped in the silicone oil, while those PCBs adsorbed onto solid particles would be retained by the filter. However, in maintaining their equilibrium vapor pressure with the surrounding air at the high flow rates used, the particulate-bound PCBs may have been entrained in the flow and swept into the vapor trap by the filters. Thus, even though only one percent of the PCB collected was retained by the filters no conclusion as to the relative concentration of PCBs in the particulate and aerosol-vapor phase is possible.

Cottonseed oil-coated glass beads and paraffin coated Chromosorb A have both been tested for a variety of pesticides. While the former system appeared promising, prolonged sampling of air resulted in partial breakdown of the cottonseed oil with the formation of electron-

Table 3.1 LIQUID PHASES ON SOLID SUPPORTS

A. HIGH VOLUME COLLECTORS

Solid Support	Liquid Phase	Reference
0.64 cm ceramic saddles	0.25 percent OV-17 silicone oil	Harvey and Steinhauer, 1974
0.3 cm glass beads	cottonseed oil	Compton and Biorkland, 1972
Florisil	5 percent glycerine	Wakimoto *et al*., 1974
Chromosorb A	5 percent paraffin oil	Seiber *et al*., 1975

B. STATIC COLLECTORS

Solid Support	Liquid Phase	Reference
0.05 cm nylon nets	30 percent glycerine in water	Risebrough *et al*., 1968
0.02 cm nylon net	silicone oil (SE-30)	Södergren, 1972
nylon nets (no dimension given)	10 percent ethylene glycol in acetone	Tessari and Spencer, 1971
glass plates	mineral oil	Young *et al*., 1975c

capturing interferences (Seiber et al., 1975). Other liquid phases (such as ethylene glycol) might prove more suitable. The trapping efficiency of paraffin oil on Chromasorb A was greater than 47 percent for most of the 23 pesticides tested in the vapor phase. There were, however, exceptions. Aldrin, for instance, was not trapped at all by this system. Therefore, one cannot be certain that this sampler would be appropriate for PCBs unless tests are conducted on specific PCB mixtures.

With the exception of the ethylene glycol coated nylon nets, all of the static collectors have been tested for PCBs.

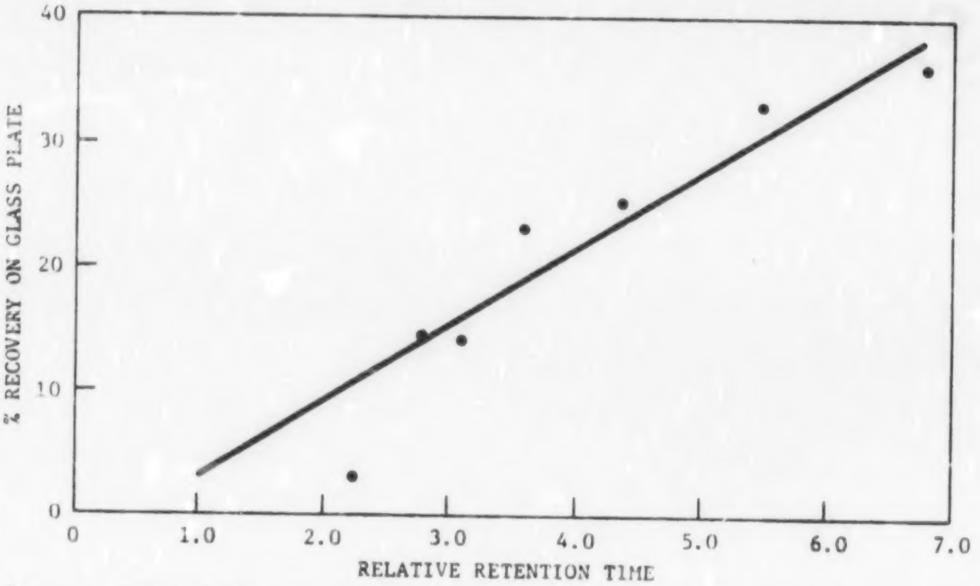
The major advantages of static collection are that the methods are noise-free, require no electrical hookups, and apparently trap about four times as much material as do impingers (Seiber et al., 1975). However, in many cases, vapors and small particulates are not collected (Risebrough, 1968; Young, 1975), and the prolonged sampling periods required for adequate collection result in significant volatilization losses (Young et al., 1975c). As was mentioned previously, in the static collection methods, the amount of air sampled remains unknown so that concentrations of PCBs at a given location cannot be computed. When these samplers are employed out of doors, variation in wind direction and speed also renders comparison among different locations or of the same location at different times quite difficult.

A type of static sampler presently in use is the mineral oil glass plate system of Young et al. (1975c). This system has undergone intensive study in order to estimate the collection efficiency for various PCB mixtures. In one experiment, a series of mineral oil coated plates were exposed for a period of eight days on a roof near Santa Monica Bay, Calfornia. The plates were divided into four groups. One group was sampled and repositioned daily; the second group was sampled and repositioned every second day; the third group was sampled and repositioned once, on the fourth day; the final group was sampled on the eighth dav only. The samples were analyzed for a variety of chlorinated hydrocarbons and a PCB mixture, corresponding to Aroclor 1254, was detected. The average total quantities of Aroclor 1254 accumulated over the eight-day period are presented in Table 3.2. The data indicate that collection efficiency decreased upon prolonged, uninterrupted plate exposure. The losses most likely resulted from volatilization. The fact that Aroclor 1242 was not detected by this method suggested that the collection efficiency was not uniform for all PCB components. In a second experiment designed to test this hypothesis, 0.1 mg of Aroclor 1242 was added to a solution of mineral oil in hexane and placed on fallout sampling plates. The plates were exposed (on the roof of the laboratory) for four days. The percent recoveries for the various Aroclor components, as a function of gas chromatographic (GC) retention time, are presented in Figure 3.3. Those components with longer GC retention times (generally the least volatile) exhibited the greatest percent recovery. The overall recovery was less than 40 percent. Since the chromatograms showed no

Table 3.2 CUMULATIVE AVERAGE QUANTITIES OF AROCLOR 1254 COLLECTED OVER AN 8-DAY PERIOD ON FOUR SETS OF COLLECTION PLATES SAMPLED AT DIFFERENT FREQUENCIES

Total Number of Collections	Aroclor 1254 (ng)
8	401
4	352
2	327
1	195

Source: Adapted from Young, D.R., D.J. McDermott, T.C. Heesen. 1975. "Polychlorinated Biphenyl Inputs to the Southern California Bight." Background paper prepared for the National Conference on Polychlorinated Biphenyls, 19-21 November, Chicago, Illinois.



Source: Adapted from Young, D.R., D.J. McDermott, and T.C. Heesen. 1975. "Polychlorinated Biphenyl Inputs to the Southern California Bight." Background paper prepared for the National Conference on Polychlorinated Biphenyls, 19-21 November. Chicago, Illinois.

Figure 3.3 RECOVERY OF AROCLOR 1242 FROM SPIKED GLASS PLATE

decomposition peak, loss through U.V. decomposition seemed unlikely. Thus, the mineral oil glass plate samplers do not adequately capture and retain the more volatile low molecular weight PCBs in the atmosphere. It is these very contaminants, however, which are most likely present in the greatest quantities.

The drawback common to all liquid-coating methods lies in the extraction of relatively large amounts of oil along with the desired compounds. These oils are difficult to separate out and interfere in subsequent analytical steps (Seiber et al., 1975).

Although a variety of liquid-coated solids are available and in use both for high volume and static air sampling, no one system efficiently and accurately traps and retains both vapor phase and particulate bound PCBs over a wide range of molecular weights.

3. Solid Adsorbents

A number of solid adsorbents have been examined in the hope that one or more of these might allow a greater rate of flow than impinger systems and less resultant analytical interference than coated solids. The solids tested for PCBs and pesticides are listed in Table 3.3. Silica gel and Chromasorb 102 were tested using the same protocol and air flow rate (~23.5 liters per minute) employed for ethylene glycol impinger sampling (Seiber et al., 1975). Trapping efficiencies towards a variety of pesticides were greater than 47 percent in all cases. A serious problem, however, was the large quantity of electron capturing background trapped from the air by the

Table 3.3 SOLID ADSORBENT SAMPLING MEDIA

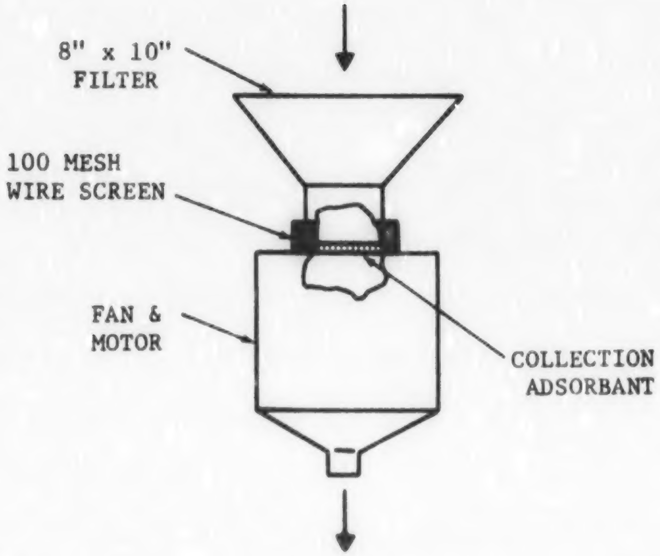
Adsorbent	Reference
Florisil	Yule *et al.*, 1971
Alumina	Stanley *et al.*, 1971
Chromosorb 102	Seiber *et al.*, 1975
Polyurethane	Bidleman and Olney, 1974
Silica gel	Seiber *et al.*, 1975

Source: Adapted from Seiber, J.N., J.E. Woodrow, T.M. Shafik, and H.F. Enos. 1975. "Determination of Pesticides and Their Transformation Products in Air," in *Environmental Dynamics of Pesticides*: 17-43, Plenum Press, New York and London.

silica gel. This background probably reflects the greater trapping efficiency of the silica gel for air constituents not trapped well by ethylene glycol.

Preliminary tests using a variety of organochlorine pesticides have also been conducted with silica gel and Chromosorb 102 at much higher air flow rates (Seiber _et al_., 1975). The device employed was a commercial high-volume sampler (Figure 3.4). The results were encouraging in that many pesticides (including the DDT compounds and the cyclodienes) were trapped with efficiencies greater than 50 percent at a flow rate as high as 1 cu m per minute. The trapping efficiency of silica gel for chlorinated hydrocarbons of high volatility was somewhat greater than that of Chromosorb 102; however, the air background trapped by silica gel was also greater. These solids have not been tested for PCBs per se.

A highly promising variation of the above sampling systems is the polyurethane foam system of Bidleman and Olney (1974a and 1974b), which has been tested for PCBs. In this system, an 8 x 10 inch glass fiber filter for particulate collection is placed on top of a container holding the solid trapping medium. The medium consists of a porous polyurethane foam plug, pre-cleaned by washing with water and extraction with acetone and petroleum ether. The entire apparatus is fitted to a high volume sampler. Since the foam offers little resistance to air passage, high airflow rates (0.4 to 0.8 cu m per minute) are easily obtained and hundreds of cubic meters of air per day may be


8" x 10"
FILTER
100 MESH
WIRE SCREEN
FAN &
MOTOR
COLLECTION
ADSORBANT

Source: Seiber, J.N., J.E. Woodrow, T.M. Shafik, and H.F. Enos. 1975. "Determination of Pesticides and Their Transformation Products in Air," in Environmental Dynamics of Pesticides:17-43, Plenum Press, New York and London.

Figure 3.4 HIGH VOLUME SAMPLER MODIFIED FOR HOLDING SOLID MEDIA

sampled. The efficiency of this collection system for tri-, tetra-, and pentachlorinated PCB vapors was found to be greater than 90 percent (Bidleman and Olney, 1974a and 1974b). In addition, this system appears to be relatively selective in that many organochlorine insecticides are not trapped by the polyurethane plugs (Enos, 1976). Selectivity provides an obvious advantage since fewer separation and cleanup procedures are necessary.

High volume sampling using some type of solid adsorption medium appears to be the best alternative for ambient monitoring of PCBs. The polyurethane foam system of Bidleman and Olney is the best solid sampling media available at this time. This system, which allows detection of PCB concentrations as low as 1 ng/m^3 in just four hours of sampling time, is presently undergoing further evaluation and optimization studies under the auspices of the Office of Toxic Substances, U.S. Environmental Protection Agency (Hochheiser, 1976).

D. EXTRACTION AND CLEANUP PROCEDURES

Removal of PCBs from the sampling medium is usually carried out by means of extraction with an organic solvent. The solvent used most frequently is hexane (Södergren, 1972; ANSI, 1974; Harvey and Steinhauer, 1974; Kutz and Yang, 1975), although use of petroleum ether, acetone-hexane mixtures, and petroleum ether-diethyl ether mixtures have been reported (Bidleman and Olney, 1974a and 1974b; Risebrough et al., 1968; Hochheiser, 1976). Since all sampling procedures trap some interfering compounds along with PCBs, some type of cleanup procedure is usually required prior to analysis. The stability of PCBs to alkali permits the removal of DDT from the extracts by saponification (U.S. EPA, 1974). Treatment with alkali converts DDT to DDE, which may then be removed by extraction with concentrated sulfuric acid. Other chlorinated hydrocarbon interferences may also be removed by this treatment (ANSI, 1974).

Column chromatography using silicic acid (silica gel), magnesia silica gel(e.g., Florisil), alumina, or some combination of these in sequence is another frequently employed cleanup procedure (ANSI, 1974).

The silica gel method was developed in 1970 by Armour and Burke (1970) and is a standard procedure for separation of PCBs from a variety of organochlorine pesticides. Careful preparation of the silica gel is required prior to use. The silica gel should be heated at 130°C for a minimum of seven hours(preferably 24 hours); the water content must then be brought to 3 percent in order to achieve the maximum margin of separation between PCBs and pesticides. Five grams of Celite should be added to every 20 grams of prepared silica gel in order to achieve a faster elution rate from the adsorbent column. PCBs are separated from DDT and its analogs by elution with petroleum ether; the DDT compounds, along with lindane, heptachlor, heptachlor epoxide, dieldrin, and endrin, may be recovered completely by a second elution with acetonitrile: hexane: methylene chloride:: 1:19:80(Armour and Burke, 1970).

Since only a small margin of separation exists between PCBs and p,p'-DDE, it is imperative that the mixture of silicic acid-celite be of a composition and activity identical to that reported in the original paper (Enos, 1976).

Elution of an activated Florisil (heated to 130°C) column with hexane removes over 92 percent of the PCBs, PCTs, DDE, heptachlor, and aldrin present in an applied extract. DDT, DDD, dieldrin, lindane, heptachlor epoxide, and endrin may then be eluted with 20 percent diethyl ether in hexane (Sherma, 1975). Some other procedure (such as saponification or silicic acid-Celite chromatography) is still, however, required to separate the DDE from the PCBs.

Alumina has been found to be a more effective, more reproducible column substrate in the separation of PCBs from electron-capturing interferences than either silicic acid or Florisil (ANSI, 1974). The activity of alumina varies considerably with age and lot; therefore, a defined amount of water (5 to 6 percent) should be added to activated alumina (heated for over four hours at 400°C) to ensure a reproducible activity (ANSI, 1974; Bidleman and Olney, 1974b). Elution of the alumina column with hexane or petroleum ether removes PCBs from interfering impurities.

E. QUALITATIVE AND QUANTITATIVE ANALYSIS

Polychlorinated biphenyls are usually determined by gas chromatography (GC) using microcoulometric, electrolytic-conductivity, or electron-capture detectors (U.S. EPA, 1974; Sherma, 1975).

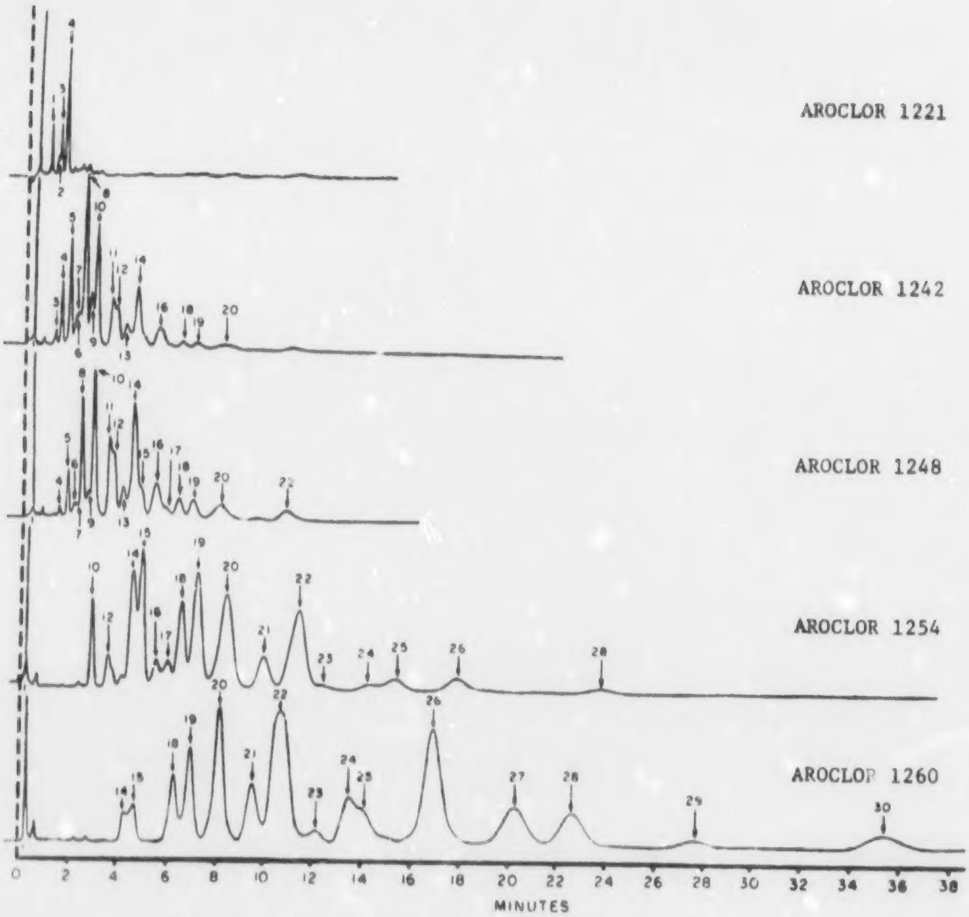
Microcoulometric and electrolytic-conductivity detectors are halogen specific so that less cleanup of extracts is required for accurate identification (Sherma, 1975; U.S. EPA, 1974). Electron-capture detectors are, however, the most sensitive (although least selective) of the three for chlorine-containing compounds. Use of electron-capture detectors is, therefore, preferred when low concentrations of PCBs (such as are present in ambient air samples) are expected. The key to successful GC analysis of PCBs is selection of a proper column. The column consists of two parts: the solid support and the liquid phase. Solid supports recommended for this work include Chromosorb W, Gas Chrom P, Gas Chrom Q, and others (ANSI, 1974; Sherma, 1975). A variety of polar and non-polar liquid phases have been investigated. The following have been found to provide adequate separation for use in PCB analysis by electron capture: DC-200, SF-96, OV-17, SE-30, QF-1, and mixtures of these (ANSI, 1974; Sherma, 1975). It is usually advisable to use at least two different columns, one polar and one non-polar, for unequivocal identification (Sherma, 1975).

Qualitative identification of residues may be made by comparing retention times for all chromatographic peaks with those of standard or commercial PCB formulations. Retention times must be relative to some arbitrary standard such as dieldrin. The various Aroclors exhibit different GC patterns useful in distinguishing between them. These differences may include the number of major peaks and the peak-height ratios of certain peaks. The electron-capture chromatograms for five

Aroclor formulations under specified conditions are presented in Figure 3.5. Due to such factors as selective metabolism, photochemical breakdown, and non-representative sampling and recovery of all Aroclor components, the GC patterns obtained from environmental samples are seldom identical to those of the Aroclor standards. Sometimes, the chromatogram clearly indicates the presence of dominant interferences or of the components of more than one type of Aroclor. In the former case, an attempt at chemical or chromatographic cleanup should be ventured. In the latter case, the PCB residues should be examined separately using the appropriate Aroclor reference for the respective portion of the chromatogram (U.S. EPA, 1974; Sherma, 1975).

Once the elution pattern has been subjectively matched to a standard PCB mixture, quantitation may be conducted by one of several methods. The total area of all accepted matching peaks in the elution pattern may be compared with the total area of the same peaks in a standard mixture of known concentration; the concentration of PCBs in the original air sample is calculated by taking the sample volume into consideration (U.S. EPA, 1975).

Other techniques for quantitation are based on the area of one or more selected peaks; total peak height, average or individual heights of selected peaks; average electron-capture detector response to biphenyls containing one to seven chlorine atoms; and determination of chlorine content of different PCB peaks with the microcoulometric detector (Sherma, 1975).



Source: American National Standards Institute. 1974. "Guidelines for Handling and Disposal of Capacitor and Transformer Grade Askarels Containing Polychlorinated Biphenyls," ANSI, C107.1, New York.

Figure 3.5 COMPARISON OF ELECTRON CAPTURE CHROMATOGRAMS FOR AROCLOR 1221, 1242, 1248, 1254, AND 1260

F. CONFIRMATION

When the quantity of PCBs in an air sample is limited, the individual GC peaks may be too small for accurate qualitative and quantitative analysis. In this case, quantitation may be effected by perchlorination of all the PCB residues to decachlorobiphenyl. Quantitative perchlorination may be achieved by incubation with $SbCl_5$ for six hours at 175°C (Armour, 1973). The perchlorinated PCB extract may then be analyzed by electron-capture gas chromatography. Quantitation is accomplished by comparison of peak area with that of a known concentration of pure decachlorobiphenyl.

Qualitative confirmation of the existence of PCBs may be obtained by thin layer chromatographic (TLC) analysis. The variety of TLC systems used for PCBs are listed in Table 3.4 (Sherma, 1975). The ratio of the distance traveled by the unknown to the distance of solvent front is compared to those of known Aroclor mixtures. Quantitation may be achieved by eluting the residues from the thin layer substrate and subjecting them to GC analysis as described above.

Although infrared and nuclear magnetic resonance spectroscopy have been used on occasion to aid in the identification of PCB mixtures, both of these methods suffer from two disadvantages: (1) lack of sensitivity and (2) requirement for a relatively pure compound (Garrison _et al._, 1972).

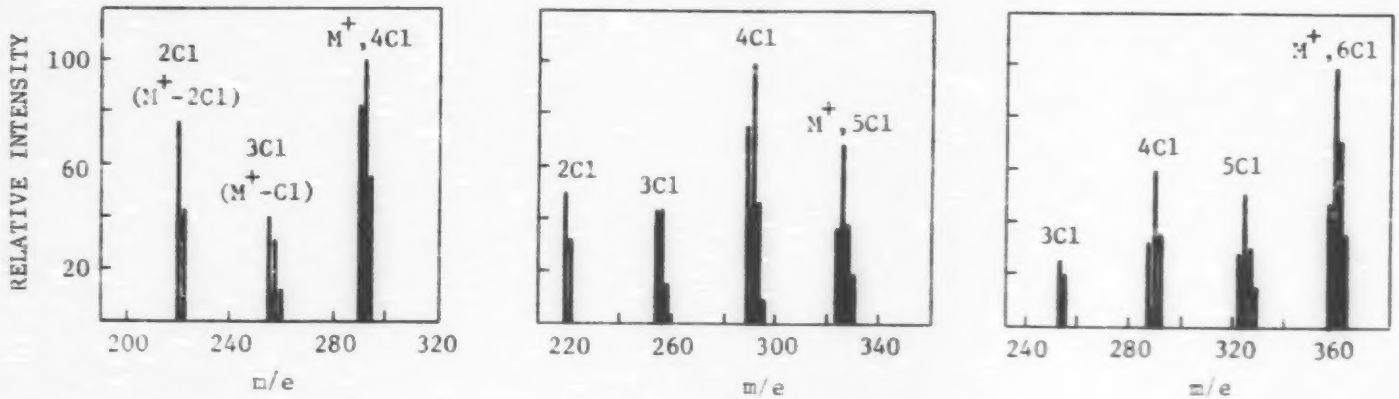
Mass spectrometry, although not in itself a very sensitive method, when coupled with gas chromatography is undoubtedly the best procedure

Table 3.4 SYSTEMS FOR THIN-LAYER CHROMATOGRAPHY OF PCBs

Layer	Solvent	Detection	Remarks
Aluminum oxide G incorporating $AgNO_3$	Benzene-hexane, 5:95	Ultraviolet light after spraying with phenoxyethanol-H_2O_2	DDE converted to DCBP by oxidative treatment; R_f PCBs=0.91-0.94, DCBP=0.30, other chlorinated pesticides = 0.48-0.88
MN-Silica gel G-HR/$AgNO_3$	n-Heptane; heptane-acetone, 98:2	Ultraviolet light	Two-dimensional development; PCBs separated from DDT and analogs
Aluminum oxide G	Hexane-anhydrous deithyl ether, 40:0.8, or pure heptane	$AgNO_3$-2-phenoxyethanol-H_2O_2 spray followed by ultraviolet light	Aldrin and DDE overlap PCB spots when development is with heptane
Liquid paraffin (8%) on kieselguhr	Acetonitrile-acetone-methanol-water mixtures	1.7 g $AgNO_3$ in 96% ethanol spray followed by ultraviolet light	Reversed-phase TLC; PCBs appear as a number of distinct spots separated from DDE, DDT, and some other pesticides

Source: Modified from Sherma, J. 1975. "Gas Chromatographic Analysis of Polychlorinated Biphenyls and Other Non-Pesticide Organic Pollutnats," Advances in Chromatography 12:141-176, Marcel Dekker, Inc.

for confirming the presence of PCB residues and characterizing the molecular composition of PCB formulations (Sherma, 1975). Coupling of the gas chromatograph and the mass spectrometer is normally carried out in such a way that a chromatogram-type readout analogous to that produced by conventional GC detectors is produced. A sample GC-MS chromatogram (that of Aroclor 1254) is presented in Figure 3.6. The fragment ion of greatest mass, in most cases, corresponds to the molecular weight of the compound, having been created by the loss of one electron. The masses of important fragment ions provide clues to the structure of parts of the molecule. Apparently, however, the primary ion spectra of different PCB isomers containing the same number of chlorine atoms are virtually undistinguishable. Therefore, the use of mass spectrometry for structural studies of PCB contaminants is fairly limited (Sherma, 1975).



Source: Modified from Garrison, A.W., L.H. Keith, and A.L. Alford. 1972. "Confirmation of Pesticide Residues by Mass Spectrometry and NMR Techniques," in Fate of Organic Pesticide in the Aquatic Environment:26-54, Advances in Chemistry Series III, American Chemical Society, Washington, D.C.

Figure 3.6 PARTIAL MASS SPECTRA (GC-MS) OF AROCLOR 1254 SHOWING THE NUMBER OF CHLORINE ATOMS ON EACH ION

IV. SOURCES

A. SUMMARY

Polychlorinated biphenyls are manufactured in many nations of the industrialized world. The sole producer in the United States is the Monsanto Company, which markets them under the trade name Aroclor. The peak of production occurred in 1970, when 7.31×10^7 pounds (3.32×10^7kg) were sold domestically. A voluntary limitation of sales by Monsanto, restricting the use of PCBs to closed-system applications, resulted in a reduction of sales in 1971 through 1974 to less than half the peak value.

Prior to 1971, PCBs were used in a wide variety of applications. Aside from their incorporation into closed system electrical devices where they served as an insulating fluid, they could be found in heat transfer fluids, hydraulic fluids, paints, protective coatings, and many other types of products where their chemical and thermal stability and non-flammability were essential. At present, the PCBs sold in the United States by Monsanto are used only for electrical applications where alternate or substitute materials are not yet available. However, PCBs may still be available for use in dispersive applications through imports, reprocessed PCB-containing waste oils, or resale by Monsanto's customers.

The greatest losses to the environment also occurred prior to 1971, when precautions against contamination had not yet been put into effect. Loss of PCBs to the environment as a consequence of use includes accidental spills, leaks, and leaching, as well as vaporization resulting from their use as pesticide extenders and in paints and plastics into which they are incorporated. As a result, several instances of gross contamination of human and animal food have been reported. Disposal of waste PCBs during production or incorporation into products was and continues to be the primary route of global contamination. PCBs are released to the hydrosphere in both municipal and industrial effluents and to the atmosphere as a result of incomplete burning or incineration.

The discontinuation of the use of PCBs in applications where the possiblity of dispersal exists, the stringent controls at production sites that have been initiated, and the imposed limitations on effluent concentrations should, if adhered to, result in a significant decrease in the amounts of PCBs released to the biosphere in the future. But evidence of negligence resulting in episodes of localized gross contamination continues to be uncovered, suggesting that even more control measures may be warranted.

B. PRODUCTION AND USE

1. Production

PCBs have been available commercially since 1929 (Hutzinger, et al., 1974) and are presently manufactured in many of the world's industrialized nations. Table 4.1 lists the major

Table 4.1 THE WORLD'S MAJOR PRODUCERS OF PCBs

Company	Country	Tradename
Monsanto	U.S.A. and Great Britain	Aroclor
Bayer	Germany	Clophen
Prodelec	France	Phenoclor and Pyralene
Kanega fuchi*	Japan	Kanechlor
Mitsubishi-Monsanto*	Japan	Santotherm
Caffaro	Italy	Fenclor
Flix	Spain	(1)
Sovol	U.S.S.R.	(1)
Chemko	Czechoslavakia	(1)

[1] No trade name given.

*PCB production has been banned in Japan since 1972 (Anonymous, Business Week, October 6, 1975).

Source: Adapted from Hutzinger, O., S. Safe, and V. Zitko, 1974. "The Chemistry of PCBs," CRC Press, Cleveland, Ohio.

producers of PCBs. The sole producer in the United States is the Monsanto Company, which markets them under the trade name Aroclor. Each Aroclor mixture is designated by a four-digit number in which the first two digits, 12, specify chlorinated biphenyl and the last two indicate the approximate weight percentage of chlorine in the mixture. Table 4.2 summarizes the total domestic production and sales figures for PCBs from 1957 to 1974 and gives a breakdown of sales by type of PCB mixture for the same period. Sales figures are presented graphically in Figure 4.1.

Over 450,000 short tons (400,000 metric tons) have been produced domestically since 1957. Although similar data for worldwide production are not available, it has been estimated that U.S. production represents approximately half of the world production (Interdepartmental Task Force on PCBs, 1972). In 1972, Japan was believed to have produced about 26 million pounds of PCB (12,000 metric tons) (Nisbet and Sarofim, 1972). However, a ban on production in that country was allegedly put into effect subsequent to that date (Anonymous, 1975a). From 1960 to 1970, U.S. domestic production and sales increased an average of 8.7 percent and 6.1 percent per year, respectively, so that both production and sales more than doubled in this decade.

By 1970, it became apparent, through monitoring efforts in both this country and abroad, that PCBs were widely distributed in the environment and might possibly pose a serious threat to a variety of life forms including man. In late 1970, Monsanto, in

Table 4.2 PCB MANUFACTURE AND SALES BY GRADE
MONSANTO INDUSTRIAL CHEMICALS COMPANY 1957 thru 1964
(Thousands of Pounds)

	1957	1958	1959	1960	1961	1962	1963	1964
U.S. Production	(1)	(1)	(1)	37919	36515	38353	44734	50833
Domestic Sales (lbs)	32299	26061	31310	35214	37538	38043	38132	44869
DOMESTIC SALES BY PCB GRADE								
Aroclor 1221	23	16	254	103	94	140	361	596
Aroclor 1232	196	113	240	155	241	224	13	13
Aroclor 1242	18222	10444	13598	18196	19827	20654	18510	23571
Aroclor 1248	1779	2559	3384	2827	4023	3463	5013	5238
Aroclor 1254	4461	6691	6754	6088	6294	6325	5911	6280
Aroclor 1260	7587	5982	6619	7330	6540	6595	7626	8535
Aroclor 1262	31	184	359	326	361	432	414	446
Aroclor 1268	--	72	102	189	158	210	284	190
Aroclor 1016	--	--	--	--	--	--	--	--

(1) Production figures unavailable during year indicated.

Source: Adapted from Monsanto Industrial Chemicals Company, 1974. "PCB Manufacture and Sales Monsanto Industrial Chemicals Company - 1957 thru 1964"(unpublished data).

Table 4.2 (continued) PCB MANUFACTURE AND SALES BY GRADE
MONSANTO INDUSTRIAL CHEMICALS COMPANY 1965 thru 1974
(Thousands of Pounds)

	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974
U.S. Production	60480	65849	75309	82854	76389	85054	34994	38600	42178	40466
Domestic Sales	51796	59078	62466	65116	67194	73061	34301	26408	37742	34406
DOMESTIC SALES BY PCB GRADE										
Aroclor 1221	369	528	442	136	507	1476	2215	171	35	57
Aroclor 1232	7	16	25	90	273	260	171	0	0	0
Aroclor 1242	31533	39557	43055	44853	45491	48588	21981	728	6200	6207
Aroclor 1248	5565	5015	4704	4894	5650	4073	213	807	0	0
Aroclor 1254	7737	7035	6696	8891	9822	12421	4661	3495	7976	6185
Aroclor 1260	5831	5875	6417	5252	4439	4890	1725	305	0	0
Aroclor 1262	558	768	840	720	712	1023	1	0	0	0
Aroclor 1268	196	284	287	280	300	330	0	0	0	0
Aroclor 1016	0	0	0	0	0	0	3334	20902	23531	21955

Source: Adapted from Monsanto Industrial Chemicals Company, 1974. "PCB Manufacture and Sales - Monsanto Industrial Chemicals Company - 1965 thru 1974". (Unpublished data.)

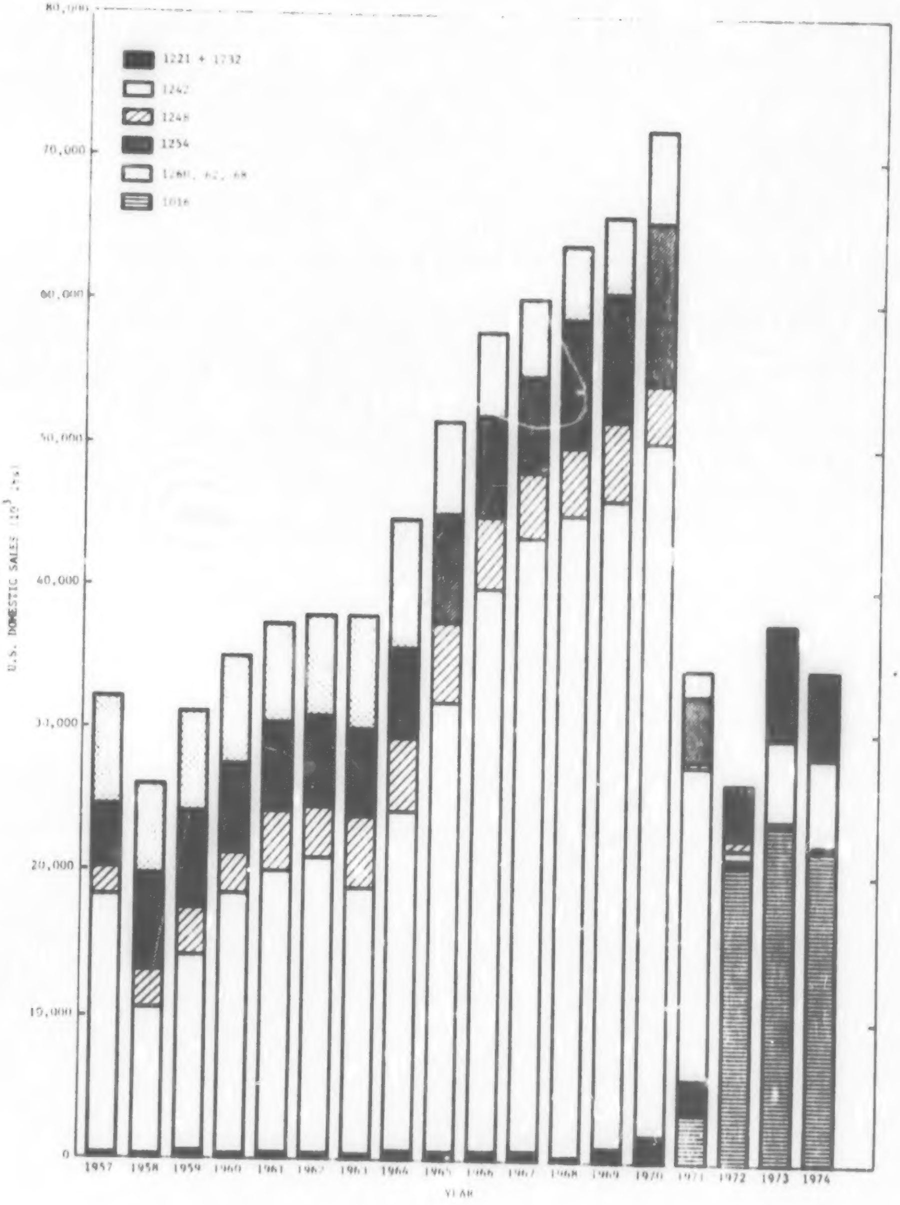


Figure 4.1 U.S. DOMESTIC SALES OF PCBs BY GRADE

response to the mounting evidence and concern, voluntarily reduced its sales of PCBs to use only in closed systems (transformer and capacitor applications) where chances of further contamination would be minimized (Monsanto, 1970). As a result, total production in 1971 dropped to 41 percent of the 1970 figure and remained below 50 percent of that figure in 1974. Monsanto subsequently developed a new grade of product, Aroclor 1016, which has largely replaced its former biggest seller, Aroclor 1242 (Monsanto, 1975a). Aroclor 1016 is 41 percent chlorine by weight (as compared to 42 percent chlorine in Aroclor 1242) but contains significantly reduced amounts of the penta-, hexa-, and hepta-chlorinated isomers, which are known to persist in the environment (Monsanto, 1972). Aroclor 1016 now accounts for 64 percent of total domestic sales. As of 1973, no Aroclor of a higher grade than 1254 has been sold. Monsanto's sales restrictions were not in response to any legal restrictions on the use of PCBs for dispersive applications.

Glenn E. Schweitzer, EPA Office of Toxic Substances, has suggested that PCBs are possibly being resold by reprocessors and by some of Monsanto's customers for unauthorized uses. (Anonymous, 1975a; Anonymous, 1975b). Although such allegations are scoffed at by representatives of Monsanto who claim that their customers "have too much at stake to do this" (Anonymous, 1975c), Thomas Kopp, a chemist at EPA's Toxic Substances Office, claims to have "received several letters confirming Schweitzer's charge." (Anonymous, 1975a).

2. Import and Export

Information as to the nature and fate of PCBs imported into this country is limited and conflicting. According to Nisbet and Sarofim (1972), imports of PCBs are primarily comprised of transformer oils and capacitor fluids in electrical devices and are thought to be small. However, according to a more recent report (Anonymous, 1975b) Glenn Schweitzer, head of the EPA Office of Toxic Substances, claims that most of the PCB imports (amounting to about 188 tons in 1974) are not used in closed electrical systems but end up in investment casting processes, heat exchange fluids and hydraulic fluids, where increased danger of loss to the environment exists. The Yates Manufacturing Company, the sole producer of the PCB-filled pattern waxes used by the investment casting industry, imports between 300,000 and 500,000 pounds of decachlorobiphenyl per year from Caffaro in Italy (Versar, 1975a). Prior to 1972, many imported resins and adhesives may also have contained PCBs as plasticizers, but the subsequent restriction of their use for such applications has probably minimized this source of entry (Organization for Economic Cooperation and Development, 1973). Another source of imported PCBs in the past was food packaging materials and, consequently, their contents. A routine survey for pesticide residues in imported food stuffs revealed 10 ppm of what appeared to be Aroclor 1242 in ground cashew nuts (Bailey et al., 1970). The lacquered cardboard drum in which these nuts were packed was found to contain 200 ppm of PCBs. It is believed that the European paper industry is no longer recycling PCB-containing paper for food packaging materials (Organization for Economic Cooperation and Development, 1973).

Domestic exports for the period 1963-1974 are presented in Table 4.3. Total exports averaged 15 percent of domestic sales during this period. Actual exports increased steadily from 3,647,000 pounds (about 1600 metric tons) in 1963 to a high of 13,651,000 pounds (62,000 metric tons) in 1970. In 1974, however, only 5,395,000 pounds (2400 metric tons) left the country.

3. Uses and Replaceability

PCBs were initially manufactured to satisfy the electrical industry's need for a fire-proof, explosion-proof insulating fluid (askarel) for transformers and capacitors. The unique physical and chemical characteristics that make them ideally suited for such use include thermal stability, non-flammability, superior dielectric properties, and resistance to hydrolysis, oxidation, acids, bases, and other chemical agents (Hutzinger et al., 1974). These same properties eventually led to the utilization of PCBs in a wide spectrum of applications. By 1970, aside from their incorporation into closed-system electrical devices, PCBs could be found in heat-transfer fluids, hydraulic fluids, machine-tool cutting oil, high-vacuum oils, specialized lubricants and gasket sealers, epoxy paints, printing inks, waxes, synthetic adhesives, textile dyes, and protective

TABLE 4.3 U.S. EXPORT SALES OF PCBs BY MONSANTO 1963-1974

YEAR	THOUSANDS OF POUNDS
1963	3,647
1964	4,096
1965	4,234
1966	6,852
1967	8,124
1968	11,231
1969	10,624
1970	13,651
1971	---
1972	6,388
1973	8,346
1974	5,395

Source: Adapted from Monsanto Industrial Chemicals Company, 1974. "PCB Manufacture and Sales - Monsanto Industrial Chemicals Company - 1957 thru 1974". (Unpublished data.)

coatings for wood, metal, and concrete, as sealers in water-proofing compounds and putty, and as plasticizers in synthetic resins and chlorinated rubber. PCBs have also been incorporated into pesticides as extenders to suppress their vaporization and prolong their "kill" time. One major use of PCBs prior to 1970 was as a plasticizer in carbonless copying paper (Fishbein, 1974). The grades of Aroclor employed for each of a selected number of applications are presented in Table 4.4. Monsanto's sales figures for the period of 1957-1974, by application, are presented in Table 4.5 and summarized graphically in Figure 4.2.

Between 1957 and 1970, 64 percent of all sales were for use in closed-system electrical applications, that is, transformers and capacitors. The remaining 36 percent were used for purposes where containment proved difficult and resultant environmental contamination was probable. The restriction of non-electrical sales by Monsanto in 1970 is reflected in their sales figures. Over 16,000 tons (14,000 metric tons) was sold for such uses in 1970; the figure dropped to 4,500 tons (4,100 metric tons) in 1971 and to zero in 1973 and thereafter. At present, Monsanto's sales are solely for electrical applications. Approximately 33×10^6 pounds per year are sold domestically for such applications. About 70 percent of the usage is in capacitor production, and, of this total, 55 percent is for small capacitors and 45 percent is for large capacitors. The remaining 30 percent (12×10^6 pounds per year), is consumed by the

TABLE 4.4 THE USES OF PCB PRIOR TO 1970

USE	GRADE(S) OF AROCLOR
Electrical capacitors	1221, 1242, 1254
Electrical transformers	1242, 1254, 1260
Vacuum pumps	1248, 1254
Hydraulic fluids	1232, 1242, 1248, 1254, 1260
Plasticizer in synthetic resins	1248, 1254, 1260, 1262, 1268
Plasticizer in rubbers	1221, 1232, 1242, 1248, 1254, 1268
Adhesives	1221, 1232, 1242, 1248, 1254
Wax extenders	1242, 1254, 1268
Pesticide extenders	1254
Inks	
Lubricants	
Cutting oils	
Carbonless copying paper	1242
Heat transfer systems	

Source: Adapted from Hutzinger, O., S. Safe and V. Zitko, 1974. "The Chemistry of PCBs", CRC Press, Cleveland, Ohio.

Table 4.5 PCB MANUFACTURE AND SALES BY CATEGORY
MONSANTO INDUSTRIAL CHEMICALS COMPANY 1957 thru 1974
(thousands of pounds)

	1957	1958	1959	1960	1961	1962	1963	1964
U.S. Production	(1)	(1)	(1)	37919	36515	38353	44734	50833
Domestic Sales	32299	26061	31310	35214	37538	38043	38132	44869
DOMESTIC SALES BY CATEGORY								
Heat Transfer	—	—	—	—	--	157	582	929
Hydraulics/Lubricants	1612	1549	2685	2523	4110	3915	3945	4374
Misc. Industrial	704	755	1569	1559	2114	1681	1528	1692
Transformer	12955	5719	5984	7921	6281	7984	7290	7997
Capacitor	17208	14099	16499	16967	15935	15382	15606	19540
Plasticizer Applications	(1)	3939	4573	6244	9098	8924	9181	10337
Petroleum Additives	—	--	—	--	--	--	--	--

(1) Production figures and Plasticizer Applications figures unavailable during year indicated.

Source: Adapted from Monsanto Industrial Chemicals Company, 1974. "PCB Manufacture and Sales, Monsanto Industrial Chemicals Company, 1957 thru 1964". (Unpublished data.)

Table 4.5 (continued) PCB MANUFACTURE AND SALES BY CATEGORY
MONSANTO INDUSTRIAL CHEMICALS COMPANY 1957 thru 1974
(thousands of pounds)

	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974
U.S. Production	60480	65849	75309	82854	76389	85054	34994	38600	42178	40466
Domestic Sales	51796	59078	62466	65116	67194	73061	34301	26408	37742	34406
DOMESTIC SALES BY CATEGORY										
Heat Transfer	1237	1766	2262	2529	3050	3958	3060	752		
Hydraulics/ Lubricants	4616	4258	4643	5765	8039	7403	1552	0		
Misc. Industrial	1841	1779	1426	1283	1079	1627	1155	0		
Transformer	8657	8910	11071	11585	12105	13828	11134	25656	37742	34406
Capacitor	23749	28884	29703	29550	25022	26708	14141			
Plasticizer Applications	11696	13481	13361	14404	16460	19537	3259	0		
Petroleum Additives	--	--	--	--	1439	--	--	0		

Source: **Adapted from Monsanto Industrial Chemicals Company, 1974. "PCB Manufacture and Sales - Monsanto Industrial Chemicals Company, 1965 thru 1974". (Unpublished data.)**

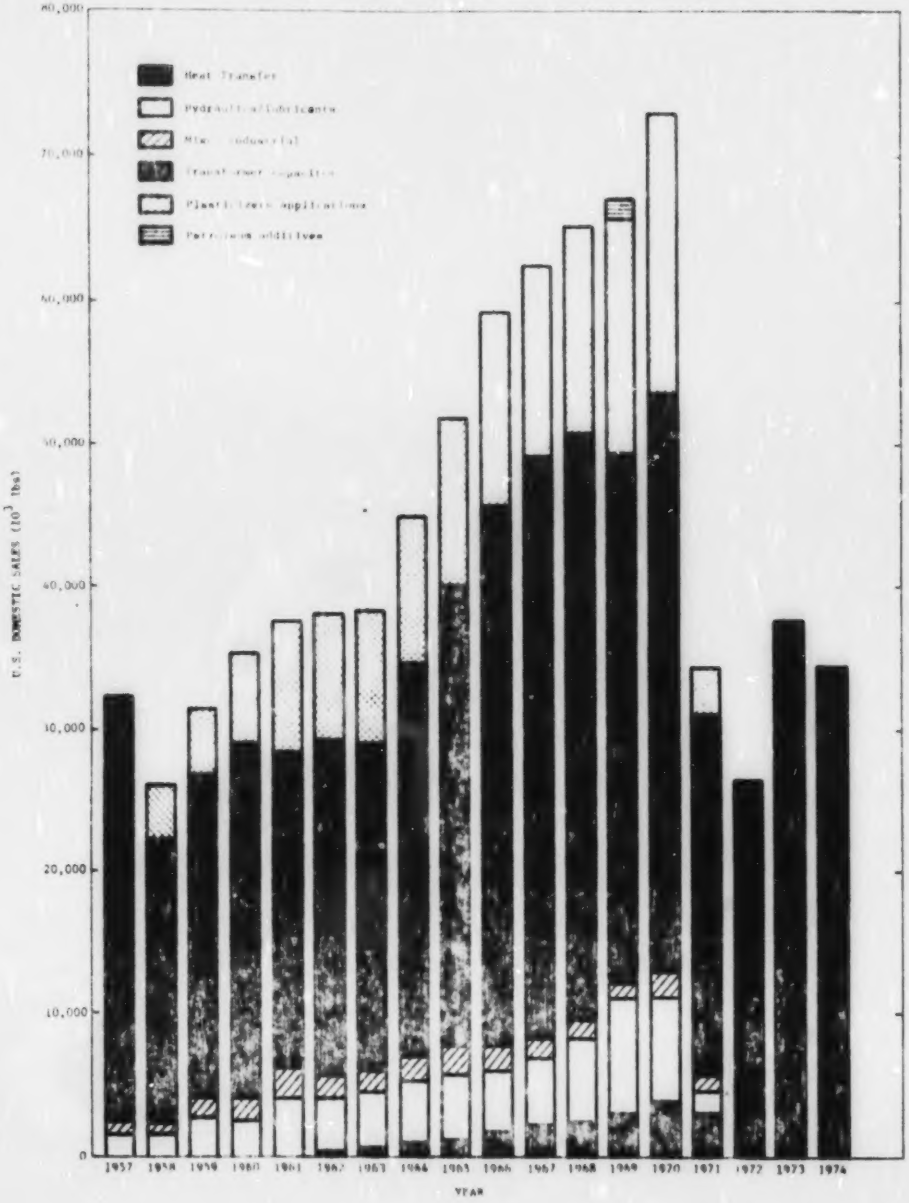


FIGURE 4.2

U.S. DOMESTIC SALES OF PCBs BY APPLICATION transformer industry with 90 percent of this amount consumed in the production of new transformers and 10 percent in the service of old units (Durfee, 1975). In 1972, Bayer of Germany followed Monsanto's lead by discontinuing the production and sales of Clophen brand of PCBs for use in all open-systems applications (Anonymous, 1973). In 1973, the Organization for Economic Cooperation and Development (OECD) agreed to restrict the use of PCBs to applications where their non-flammability was an essential factor (OECD, 1973). Their agreement is less restrictive than Monsanto's program since they allow the use of PCBs for non-food-related heat-transfer fluid applications and for hydraulic fluid in mining equipment (Monsanto, 1974c). Although the use of those PCBs produced domestically appears to be restricted to non-dispersive applications, no such regulation is in effect for imported PCBs. One major application of a specific type of imported PCB (decachlorobiphenyl) is as a filler in investment casting waxes. About 400,000 pounds of decachlorobiphenyl are imported annually from Caffaro in Italy by the Yates Manufacturing Company in Chicago, Illinois, which produces approximately 1.5 million pounds of PCB-containing wax per year. Decachlorobiphenyl constitutes approximately 30 percent of the weight of the wax (Durfee, 1975; Versar, 1975a). Yates is the sole producer of this type of investment casting wax although four other companies produce waxes containing polychlorinated terphenyls (PCTs) (Versar, 1975a). There are currently 135 investment casting foundries in the United States, 25 of which use PCB-containing wax.

The investment casting process is a lost wax casting process. A pattern is molded by the injection of the molten casting wax into a metallic die where the wax cools and solidifies to form the desired shape. The wax pattern is then surrounded by a slurry containing a refractory ceramic (known as the investment) to form the final mold. After the mold dries to an appropriate strength, the wax pattern is melted in an autoclave and the wax is recovered for possible future use or disposal. Residues of wax remaining in the pores of the ceramics mold are burned out in a furnace at 1900 to 2000° F. Molten metal may then be poured into the cavity of the ceramic mold to form a casting (Versar, 1975a). Addition of fillers such as PCBs or PCTs to investment casting waxes is a development of the last decade. By reducing the wax content through addition of low shrinkage fillers, volumetric shrinkage of the ceramic mold may be controlled (Versar 1975a).

A source of considerable concern was discovered with the identification of PCB residues in a variety of human and animal food and feed (Interdepartmental Task Force on PCBs, 1972). The use of coatings containing PCB as silo sealants and the recycling of PCB-containing carbonless carbon paper for food packaging are examples of the means by which such contamination came about. The major European producer of carbonless carbon paper (Wiggins Teape) discontinued the use of PCBs in its product as of June 1970 (Lister and Bennett, 1972) and the American producer (National Cash Register) followed suit exactly one year later (Trout, 1972). Although the levels of PCBs in paperboard have decreased since these measures were taken, 6 percent of samples of paperboard used in Canadian food packaging were found to contain in excess of 10 ppm PCB when analyzed in 1973. About 20 percent of the samples contained between 1 and 10 ppm (Villeneuve *et al.*, 1973).

The Food and Drug Administration, with the support of the Department of Agriculture, has tightened controls over the use of PCBs for any purpose that might result, directly or indirectly, in the contamination of the food supply. Surveillance measures have been put into effect to ensure that PCBs are not used on farms, in food plants, or in food-packaging material (U.S. Department of Health, Education and Welfare, 1972).

Alternate or substitute materials are available that can replace PCBs in many of their former uses (Interdepartmental Task Force on PCBs, 1972). Tricresyl phosphate and other phosphate esters are frequently used as hydraulic-fluid additives and serve adequately as vacuum-pump oils. Non-flammable fluids, which can be employed in heat-transfer applications, include fluorocarbons, water, and molten salts and metals. A wide variety of plasticizers are available depending on the specific property required, and the phthalate esters have replaced PCBs as general-purpose plasticizers. In 1972, Bayer, in Germany, announced the development of two experimental products known as Leromoll L2279 and L2280, which are mixtures of entirely synthetic aliphatic and aromatic hydrocarbons of medium molecular weight with properties similar to Clophen. Their intended use is in the manufacture of chemical-resistant paints, sealing and joint-filling compounds, adhesives, and printing inks (Anonymous, 1973). Alternatives to the use of decachloro biphenyl as a filler in investment casting wax include use of a substitute filler or of an unfilled wax. The properties required for a filler are: a melting point exceeding 300°C, a high heat-transfer coefficient, a low thermal coefficient of linear expansion, and "zero" ash (Versar, 1975b). Isophthalic acid, one possible candidate, was found to leave an ash residue upon testing. A recently commercialized grade of isophthalic acid exhibited a much lower ash content; its cost is comparable to that of decachloro biphenyl (Versar, 1975b).

Industry claims that reverting to the use of unfilled waxes will increase production costs by about 10 percent. However, new types of unfilled waxes are presently available whose properties are supposedly equivalent to those of the PCB-filled waxes and whose cost is somewhat lower. The exact formulation of these waxes is not known (Versar, 1975b).

The only application of PCBs for which no suitable substitute is presently commercially available is also their major application--as electrical insulating and cooling fluids in transformers and capacitors. The PCB-containing fluids (known as askarels) are used when the electrical equipment is installed in or near buildings, as they are virtually free from the danger of fire and explosion. While mineral oil, another frequently used insulating fluid, has a flammability rating of 10-20 (based on a value of 0 for water and of 100 for ether), Aroclors 1242 and 1016 have a rating of 2-3 (Interdepartmental Task Force on PCBs, 1972). Thus, when power surges occur, the resultant arcs will vaporize and ignite mineral oil, whereas PCBs will safely withstand temperatures of up to 1600°F. (Anonymous, 1971). Mineral oil is, therefore, dangerous to use where failure of equipment and resulting fire might present a potential danger to life and property.

Equipment containing PCBs is also more reliable and longer lasting. Small PCB-impregnated capacitors have a life expectancy of 10 to 15 years, while large capacitors last between 20 and 25 years. PCBs in transformers need to be replaced only every 25 to 30 years. Only 5 percent of all transformers contain PCBs; these are located primarily in or near buildings or transportation facilities.

The amount of askarel contained in a transformer varies with transformer size. The Interdepartmental Task Force on PCBs (1972) reported that the quantity ranges from 40 to 500 gallons (150 to 1890 liters) which weighs 516 to 6450 pounds (235 to 2932 kilograms), the average being 235 gallons (890 liters) weighing 3032 pounds (1378 kilograms). However, the largest askarel-containing transformer now in use in Richmond by Virginia Electric Power Company holds about 600 gallons (2271 liters) (Lewis, 1976), and a transformer of the Chicago Transit Authority contains 800 gallons (3028 liters) (Willmore, 1976). Furthermore, Hall (1976) mentioned several transformers that hold in excess of 1000 gallons (3785 liters) and one with a content of 1500 gallons (5675 liters). Hall and Haigh (1974) reported that transformers can contain thousands of gallons of askarel.

PCBs are used in over 90 percent of the large power-type and smaller industrial-type capacitors presently manufactured. PCB-impregnated capacitors are more reliable, longer-lived, and one-sixth the size, one-fifth the weight, and one-fourth the cost of similar oil-impregnated capacitors. Capacitors used for lighting and air-conditioning purposes contain 0.0005 to 0.09 gallons (0.002 to 0.34 liters) of PCB each. The largest power capacitors contain about 6.7 gallons (25 liters) of askarel. (Interdepartmental Task Force on PCBs, 1972) It is claimed that, if PCBs were no longer available for this equipment, the time, money, technological advances, etc., required to replace them would result in a very serious disruption of the nation's electrical system.

Dow Corning Company and Dow Chemical Company claim to have developed alternatives to PCBs for use in both transformer and capacitor applications respectively. The Dow Corning substitute to be used in transformers is a polydimethyl siloxane liquid known as "200 fluid" (Anonymous, 1975c; Mason, 1975). The product has been on the market for about four months and is extremely thermally stable, less explosive than PCBs, but is slightly more flammable. The Japanese railroad system has made use of "200 fluid" for the past four years, and field evaluations are currently in progress in Scandinavia, Britain, and France. The substitute to be used in capacitors is an alkylated chlorodiphenyl oxide which Dow Chemical hopes to commercialize by early 1976. The diphenyl oxide is only suitable for power-factor-correction capacitors of the type used by public utilities. These capacitors constitute an extimated 25 percent of the total domestic market for PCBs (McStrock, 1976). Although a 300 percent increase in the price per unit weight of fluid is expected to accompany the substitution of the Dow Chemical product for PCBs (Lokey, 1975), the cost of the capacitor itself would only increase from 10 to 20 percent (McStrack, 1976); however, Dow claims that due to better performance, total operating costs would be reduced. One capacitor manufacturer (McGraw-Edison) has been testing this substitute insulator for about a year. General Electric is using a phthalate ester as the base for a non-PCB impregnant for capacitors (Richel, 1974). The G.E. product, known as Econol, is presently used in that company's exports to Japan where PCBs are now banned.

Monsanto also claims to be working on alternatives to PCBs for electrical insulation (Anonymous, 1975c) and Japan's Nippon Petrochemical Co. is marketing various types of naphthalenes as replacements for PCBs in capacitors (Anonymous, 1975a). Contrary to the fears of many electrical-industry spokesmen, no accidents directly related to the ban on PCBs in Japan have been reported since the ban went into effect in 1972 (Anonymous, 1975a).

C. LOSSES TO THE ENVIRONMENT

1. Losses During Production, Transport, and Storage

Spills and losses of PCBs during production and transportation prior to 1970 are difficult to estimate, although Monsanto claims they have been negligible (Monsanto, 1970). However, the high level of PCBs in catfish found in waters near Anniston, Alabama, one of the two locations at which PCBs have been produced in the United States, constitutes evidence that effluents from the plant contained high levels of PCBs (Nisbet and Sarofim, 1972).

Since 1970, Monsanto has initiated a comprehensive program to control losses during production and transport (Monsanto, 1973a). A drainage system has been installed in the production area so that any material accidentally spilled will eventually be collected in one of two 3,000-gallon settling basins. Discarded materials are either stored or incinerated at 2000°F, a process which reduces them to CO_2, H_2O, and HCl (the latter is removed prior to venting). All rupture disc lines and atmospheric vents have been rerouted through catch tanks or redirected to settling basins. Traps for leaks have been installed at all sampling points. All air and gas that escape the plant are passed through a Brink Mist Eliminator and vents are continuously monitored. In addition, process temperatures were lowered to minimize vaporization. Underground sewers were replaced with above-ground sewers and effluents are monitored with equipment accurate in the parts-per-billion range.

Losses from the company's production unit into wastewater effluents are presently estimated at less than one half pound per day and that water is subsequently treated by a municipal plant. By the time the water reaches the Mississippi River, the amount of PCBs remaining is in the parts-per-trillion (ppt) range. Monsanto is providing clothing for its workers and is incinerating the fluid used to clean it (Anonymous, 1971). Loading and shipping safeguards have also been established with specific instructions written on every container shipped. Inspections of customers' unloading facilities are periodically made to ensure that adequate precautions against spills are being taken. It is unlikely that such comprehensive precautions are taken by the manufacturers of PCB-containing products. Sampling of ventilation stacks at a General Electric Co. capacitor manufacturing plant which had been using Aroclor 1016 for one year showed PCB levels of 0.4 ppm (about 470 $\mu g/m^3$) with the range being 0.2 to 0.6 ppm. A detailed description of the ventilation system was not available. Samples of air taken 2 to 3 miles from the plant showed no detectable PCB levels but the limit of sensitivity is not known (Levitz et al., 1973).

2. Losses During Use

Except for their application as pesticide extenders, PCBs were not intended to be discharged into the environment. Their presence in the environment as a consequence of use was entirely accidental. Due to their immediate and obviously disasterous effects, the most notorious episodes were those which resulted in contamination of the food supply. However, of greatest significance from the point of view of atmospheric contamination are those losses resulting in either direct release to the air or release to land or water where evaporation and codistillation may occur (see Sections V.D.1 and V.D.2).

Examples of pathways by which PCBs entered the environment prior to 1970 are:

(a) Through vaporization from PCB-containing paints, coatings, and plastics, etc., Nisbet and Sarofim (1972) have estimated that 10 to 20 percent of the PCBs sold domestically for plasticizer applications during 1970, or 1 to 2 x 10^3 metric tons, were lost to the environment through vaporization. Assuming that sales distributions were approximately the same since 1930 and that cumulative sales in the U.S. over the period 1930 to 1970 were about 500,000 tons (454,000 metric tons), close to 30,000 metric tons of PCBs have been released to the atmosphere by this pathway. Some specific PCB-containing surfaces that are distributed throughout the United States and that may be a continuous source of atmospheric contamination through vaporization in sunlight include asphalt pavements (black top) made with PCB-containing waste oil, old roofing tile also made with scrap oil, and highways whose lane dividers were painted with PCB-containing paints (Papageorge, 1975).

(b) Improper use of discarded transformer fluid (Interdepartmental Task Force on PCBs, 1972). Discarded transformer fluid was used as a vehicle for an herbicide sprayed along a power-line right-of-way near Martinsburg, West Virginia. The PCBs contaminated a dairy cattle grazing area and were subsequently found in milk. It is probable that release to the atmosphere also occurred during this episode.

(c) Migration and leaching from surface coatings and packaging materials.

1. PCBs were frequently incorporated into the formulation of paints and sealants used on silo walls. The silage became contaminated as a result of dislodged wall chips or PCBs leaching into the silage juices. In one study (Skrentny et al., 1971), gas chromatographic analysis of silo wall chips showed a pattern identical to that of Aroclor 1254. Table 4.6 summarizes the results of analyses of silage from three farms as a function of distance from the contaminated wall. The greatest amount of contamination was found in material collected within the first six inches of the wall. Residues declined rapidly as the distance from the wall increased, with none being detected four feet from the wall. On Farm C, newly stored silage showed only slight contamination two to four inches from the wall. After six months, the contamination in this area increased almost 50-fold, indicating that leaching into silage juices had occurred.

A later study (Savage et al., 1973) on pit silos (as well as upright silos) covered with plastic sheets containing PCBs revealed contamination in two out of 31 silage samples. Values ranged from 0.04 to 0.08 ppm PCB.

TABLE 4.6 PCB RESIDUES (PPM)* IN SILAGE

Farm	Silo wall chips	Inches from Wall 0-2	2-4	6-12	12-24	36-48	48-72
A	10	0.00	0.00	0.00	0.00	0.00	0.00
B	10,000	24.31	4.02	0.27	0.15	0.13	0.00
C	2,000	31.43	0.07	0.10	0.10	0.00	0.00
C**	2,000	15.04	3.40	0.13	0.00	0.00	0.00

* Limit of sensitivity = 0.02 ppm

** Six months after silage placed in silo.

Source: Skrentny, R.F., R.W. Hemkin, and H.W. Dorough. 1971. "Silo Sealants as a Source of Polychlorinated Biphenyls (PCB) Contamination of Annual Feed." Bulletin of Environmental Contamination and Toxicology 6(5): 409-416.

These PCBs eventually ended up in the human food supply. In 1970, milk from dairy farms in Ohio, Georgia, and Florida was found to be contaminated as a result of PCBs from silo sealants leaching into the cattle feed.

Willett has pointed out that residues continue to appear in silage many years after the coating is applied and long after all visible traces of coating are gone (Willett, 1974a,b). PCB residues were observed in silage from a silo coated 16 years previously. Thus, even though paints with PCBs are presently prohibited from use in silos, the danger of contamination from old silos still exists. The Food and Drug Administration recognized this problem and established a temporary tolerance of 2.5 ppm on a fat basis for PCB residues in milk (U.S. Department of Health, Education and Welfare, 1972). Dairymen must presently face the choice of losing money from unsalable milk or replacing their silos. Willett tested a series of coating materials to determine if they could provide a barrier to PCB residues. Hydraulic cement with an acrylic bonder and water-carried epoxy were extremely effective. Wall scrapings and silage prior to recoating with the former material contained 20,155 ppm and 103 ppm PCB, respectively. After recoating, silage contained 0.24 ppm and 0.10 ppm on two successive analyses. Concentrations in milk from cows fed these silages were well below the 2.5 ppm temporary tolerance established by the Food and Drug Administration. One year after coating, the concentration in milk was 0.075 ppm.

2. A study by the Food and Drug Administration (Interdepartmental Task Force on PCBs, 1972) revealed that 67 percent of food packaging samples tested were positive for PCB residues, with the highest value reported at 338 ppm. Nineteen percent of the foods from these packages contained PCB residues at an average concentration of 0.1 ppm and an upper limit of 5 ppm. Derived from carbonless copying paper recycled into food-packaging material, the PCBs probably migrated to the food through physical contact and vaporization. PCB-containing food wraps managed to contaminate human food indirectly when bakery goods so packaged were ground up, packaging included, and fed to poultry intended for human consumption. PCB residues in the poultry fat were as high as 26.9 ppm. The eventual destruction of both the original carbonless copying paper and that recycled into food packaging was, and is, probably through burning or incineration, thus releasing large quantities of PCBs directly into the atmosphere.

3. Jensen (1972) has estimated that 80 to 85 percent of all small boats and 50 to 60 percent of the larger ships in Sweden have been coated with paint, containing 3 to 5 percent PCB, on surfaces below the water line. Plankton samples collected in the wake of such a boat were strongly contaminated with PCB from the bottom paint (Jensen et al., 1972). In one sampling, there was a 14-fold difference in concentration of PCB between plankton taken in the wake (170 ppm) and plankton taken from the side of the boat (12 ppm). It is suggested that extensive and continuous loss of PCB from boats is contributing significantly to the pollution of Swedish water.

The waterways of the United States may also have experienced contamination with PCBs from painted boats in the past. However, evidence suggests that use of PCB-containing antifouling paints is declining. Because of the extensive use of recreational, commercial, and naval vessels off Southern California, the Southern California Coastal Water Project conducted a study of the PCB content of paints used in boats docked in marinas and harbors along this coast (Young et al., 1974). Of 28 samples of commonly used paint, seven contained PCBs corresponding to Aroclor 1242 and/or 1254 with median concentrations of 0.3 and 0.7 mg/liter, respectively. From estimates of the number of boats docked in the area, the percentage painted each year, and the quantity of paint applied per boat, it was calculated that for the entire fleet less that 300 grams of PCBs are applied to boat bottoms each year. The fact that much larger quantities were used in the past was deduced from examination of paint scrapings from boats in Southern California drydocks. Concentrations of Aroclor 1242 ranging from 20.1 to 3,000 mg/dry kg and of Aroclor 1254 ranging from 0.3 to 150,000 mg/dry kg were detected. These boats are still releasing PCBs to the hydrosphere and contaminating the food chain. Aroclor 1254 levels in bay mussels from the interior regions of harbors where bottom scraping and repainting facilities are situated were as high as 0.9 mg/wet kg as compared to 0.05 mg/wet kg from outer control regions. Since vaporization from paints and painted surfaces represents a recognized source of PCBs in the atmosphere, direct contamination by this route may be occurring continuously. Monsanto has not sold PCBs to paint manufacturers since 1970. It is not known whether the low level PCB-containing paint now in use is left over stock from 1970, is imported, or is produced from PCBs obtained from sources other than Monsanto.

(d) Leaks from heat exchangers and partially sealed hydraulic systems.

1. Leakage from a heat-exchange system used for pasteurization of fish meal at East Coast Terminal in Wilmington, North Carolina, resulted in extensive contamination of the fish meal with Aroclor 1242. As a result, poor hatchability of chicken eggs was noted at Holly Farms, Wilkesboro, North Carolina, and one poultry producer had to destroy over 88,000 contaminated broiler chickens.

2. In 1968, leakage from a heat-exchange system contaminated rice oil in Japan with Kanechlor 400, a PCB mixture containing 48 percent chlorine (Edwards, 1971; Jensen, 1972). About 1,000 people were eventually affected and many of them became seriously ill. The oil itself was found to contain levels of 2000 to 3000 ppm; the average amount of oil ingested resulted in human exposure to a total dose of 2 g (Kuratsune _et_ _al_., 1972).

3. Residues of Aroclor 1254 were identified in sediment, oysters, fish, blue crabs, and shrimp in Escambia Bay near Pensacola, Florida (Duke _et_ _al_., 1970). The source was the effluent from a local

industrial plant which was accidently contaminated through leakage of hydraulic fluid from an air compressor*.

(e) Certain types of ballasts used in fluorescent-light fixtures contain PCBs. When they burn out, leaking and smoking occurs. Although newer ballasts have thermal protective cut-out switches which prevent overheating and the consequent leaking and smoking, the older types are still in service in many offices, laboratories, and industrial plants as well as some homes. A study to determine the extent of contamination of the air surrounding a newly burned-out ballast with PCB was performed (Staiff _et al._, 1974). Highest values were found in air directly below the fixture, at the nose-level of workers in this particular laboratory. All values, however, were well below 1 ppm. PCBs were still detectable at very low levels three days after the burn-out. Analysis of the oily liquid which dropped from the ballast revealed 6.2×10^5 ppm (62 percent) Aroclor 1242.

At present, domestic sales of PCBs are restricted to closed system applications where chances of loss to the environment through use are slim. Most of the sources of accidental loss cited above are presumably no longer in existence or are in the process of being phased out.

Losses in use continue to occur in the investment casting industry (see Section IV.B.3). In the manufacture of the wax, the decachlorobiphenyl is added in powdered form to the wax base. Losses of PCB dust to the atmosphere are expected to take place both in the process of powdering the PCBs and in the mixing itself (Versar, 1975a).

---

*The article states that the leak came from a heat exchange system but further evidence revealed that an air compressor was at fault (Nisbet and Sarofim, 1972).

The nature of the casting operations also provide a great potential for environmental loss. During mold production, the wax is melted and injected into metal dies. Significant quantities of wax dust and fumes may escape during this process. The melting of the wax in a steam autoclave also results in emission of PCBs to the atmosphere. Furthermore, if the wax is reclaimed, the water imparted to the wax during the autoclave procedure is removed by evaporation at high temperature, further contributing to contamination of the atmosphere.

Another operation leading to atmospheric contamination is the removal of wax residues from the ceramic mold by firing in a furnace at 1900 to 2000°F. Vapors from all sources leave the plant with the stack gases or through the foundry air exhaust system and result in contamination of the ambient air as well as the industrial environment (Versar, 1975a). Losses to the hydrosphere, possibly through contact with cooling water, may also occur. An effluent sample from an investment casting plant in Michigan was found to contain 2.5 μg/l of PCB (Hesse, 1975).

3. Disposal

Disposal of waste PCBs and products containing them is undoubtedly the major source of environmental contamination. Various methods of disposal, which may result in significant loss to the environment, include:

(a) Open burning or incomplete incineration of municipal and industrial solid wastes.

(b) Allowing fluids containing PCBs to flow into waterways with municipal and industrial waste effluents, treated as well as untreated.

(c) Dumping of sewage sludge, municipal and industrial solid waste, and dredge spoil at sea.

(d) Dumping solid waste and sewage sludge on land in sanitary landfills and dumps.

Due to vaporization and codistillation, all of these disposal methods are potential sources of PCBs in the atmosphere.

The unique chemical stability of PCBs prevents their being destroyed by the usual waste incineration methods (Gustafson, 1970). Under these conditions, PCBs do not burn, but vaporize. They are subsequently carried into the atmosphere where they adsorb onto particulates and return to the surface of the earth. It is believed that the PCBs detected in the waxy layer on the needles of pine trees around Stockholm are a result of vaporization due to incomplete incineration or open burning of PCB-containing waste (Jensen, 1972). Certain PCB-containing products are especially dangerous to burn because of atmospheric contamination. For instance, PCBs are detectable 100 miles downwind from a burning car. Incomplete incineration of recycled PCB-containing paper and food packaging would be expected to release large amounts of these chlorinated hydrocarbons (Young, 1975). Incineration at 2000°+ F. for two seconds, however, will completely destroy

PCBs. To meet the problem of disposal of scrap liquids, Monsanto has set up a special incinerator and made incineration services available to all of its customers (Monsanto, 1973; ANSI, 1974). The incinerator can accomondate 10,000,000 pounds (4,500,000 kilograms) per year. One year after the announcement that such a service was planned, 500,000 pounds (227,000 kilograms) of waste PCBs had accumulated at the disposal site (Nisbet and Sarofim, 1972).

Municipal incinerators, which may unknowingly handle PCB-containing refuse, most likely do not reach the extreme temperatures necessary to decompose these compounds and may be releasing them to the atmosphere in large amounts. PCB residues were detected in two samples of fly ash from particulate control devices of incinerators in Pennsylvania and New Orleans indicating incomplete destruction (Carnes et al., 1973). Thus, PCBs may also enter the atmosphere adsorbed to particulate matter emanating from incinerators with inefficient or no particulate controls.

Combustion of coal represents another possible route of PCBs into the environment. PCBs were recently detected in the flue gases of a representative coal-fired utility boiler (Cowherd et al., 1975). The test facility was a 125-MW boiler at the Tennessee Valley Authority Widows Creek Steam electric generating station. According to Ronald Venezia of the EPA, there exists some question as to whether these PCBs were formed in the combustion process, resulted from the dumping of waste transformer oil on coal piles, or were generated as an artifact of the analytical system. Further analytical work is planned in other power plants to confirm these preliminary results. In addition, the Widows Creek samples will be subjected to additional analysis at another laboratory to verify the original findings (Venezia, 1976). Should subsequent findings indicate that PCBs are indeed formed in the combustion process, coal-fired power plants would represent a significant source of atmospheric PCB pollution.

The discharge of PCB-containing liquid wastes into inland and coastal waters constitutes a serious source of contamination. Both municipal sewage-treatment outfalls and industrial waste-water effluents are responsible. An additional minor source is the dumping of sewage sludge at sea (Interdepartmental Task Force on PCBs, 1972). Approximately 4,000,000 tons (3,630,000 metric tons) of sludge per year are deposited into the Atlantic Ocean and the Gulf of Mexico, and estimates of sewage sludge contamination ranging from 2.5 to 15.6 ppm have been reported (Interdepartmental Task Force on PCBs, 1972; Hesse, 1975). Based on these estimates, it may be calculated that between 10 and 62.4 tons (9 to 57 metric tons) of PCBs reach the ocean annually by this route. Nisbet and Sarofim (1972) estimated that between 1930 and 1970, 60,000 tons (54,000 metric tons) of PCBs were deposited into the waterways of the United States from all sources. Because of their very low aqueous solubility, PCBs discharged into a river, lake, or coastal water will accumulate in the sediment in high concentration and redissolve very slowly (Fishbein, 1974). Thus, they present an immediate threat to life at the bottom of bodies of water and a chronic threat to life in the water. The highest concentrations of PCB residues in freshwater fish occur in rivers that are associated with industrialized areas. Concentrations ranging from 13.4 ppm to greater than 100 ppm have recently been found in fish in the Hudson River (Richardson, 1975). The source of this gross contamination was traced to the General Electric Company (G.E.) which operates two plants on the river about 60 miles north of Albany. G.E. has admitted to dumping as much as 30 pounds per day into the Hudson and claims that this figure may have been even higher in the past. In response to pressure from both the New York State Environmental Conservation Department (which seeks zero discharge of PCBs from G.E. into the Hudson by September 30, 1976) and the United States Environmental Protection Agency (which stipulates a limit of 99.84 g/day by 1977), G.E. has, for the present, managed to reduce its discharge to approximately 2000 g/day. However, Ogden Reid, New York State Environmental Commissioner, says that irreparable and irreversible damage may already have been inflicted on the river (Richardson, 1975). Tables 4.7 and 4.8 summarize data that has been collected on actual PCB concentrations in industrial waste-water effluents and municipal sewage-treatment-plant outfalls, respectively. Veith and Lee (1971) claimed that the occurrence of significant concentrations of PCBs in municipal waste constitutes evidence that PCBs were widespread and possibly present in consumer products.

Table 4.7 PCB CONCENTRATIONS IN INDUSTRIAL EFFLUENTS

Location	Kind of Industry	Date	Aroclor Compound Detected	Concentration in Effluent (ppb)	Source of Data
Saukville, Wisc.	Chemical Plant	3/70	1242	2.50	Vieth and Lee, 1971
Ohio - Great Miami River	Paper Coating Company	1/71	1242 and 1248	27	EPA data - Analytical Quality Control Lab
	Paper Treatment	1/71	1242	430, 470*	"
	Appliance	1/71	1254	5	"
	"	1/71	1254	18	"
Florida-Escambia River	Chemical Plant	4/69 - 10/69	1254	2.5-275	Duke et al., 1970

* Samples from treatment lagoon.

Spurce: Interdepartmental Task Force on PCBs. 1972. "Polychlorinated Biphenyls and the Environment." (Com-72-10419), Washington, D.C.

TABLE 4. CONCENTRATION OF PCBS IN MUNICIPAL SEWAGE TREATMENT PLANT OUTFALLS

Collection Site	Collection Date	Aroclor Compound Detected	µg/l (ppb)	Flow per Day Mgd[1]	Est. PCB Discharged per day (lbs)	Source of Data
Ohio-Miami River						
Dayton	1/19/71 0800 to 1/20/71 0800	1254	17	48	6.2	EPA Unpb. Data
Hamilton	1/19/71 0000 to 1/19/71 2400	1248	10	8	0.6	"
Middleton	1/19/71 0800 to 1/20/71 0800	ND*		--	--	"
Wisconsin-Milwaukee River						
West Bend	3/26/70	1254	0.25	1.4	0.002	Veith & Lee, 1971
Fredonia	"	1254	0.12	0.1	0.002	"
Saukville	"	1260	0.13	0.1	0.002	"
Grafton	"	1254	0.04	0.8	0.002	"
California						
East Bay (San Francisco)	12/70	1254	3.1-3.8	155	4.2	Schmidt *et al.*, 1971
San Francisco	"	1254	3.8-5.8	31.5	1.2	"
Terminal Island	"	1254	5.8-12.8	9.3	0.7	"
Orange County	"	1254	0.21-0.64	130	0.4	"
Hyperion	"	1254	0.16-0.37	340	0.7	"
White Point	"	1254	76	350	213	"
Richmond		ND*		--	--	
San Diego		ND*		--	--	
Oxnard		ND*		--	--	

[1] Mgd = million gallons per day (8,000,000 lbs/day)

ND - not detected

Source: Interdepartmental Task Force on PCBs, 1972. "Polychlorinated Biphenyls and the Environment", (Com-72-10419), Washington, D.C.

A recent study designed to determine the major sources of PCBs in the marine ecosystem off Southern California revealed some surprising results (Young et al., 1975a, 1975b). The primary source appears to be the submarine discharge of municipal waste water effluents. All major municipal waste water systems release the PCBs in similar quantities (1 to 3 metric tons per year) and the total loss for the year 1973-1974 was 6.5 metric tons. Evidently, direct release from industrial sources in this area is insignificant. Also, 80 percent of the PCBs released via municipal effluents consisted of Aroclor 1242, the remaining 20 percent consisting of Aroclor 1254 (Young and Heesen, 1975).

Another study of waste water effluents from eleven Wisconsin cities is summarized in Table 4.9 (Dube et al., 1974). One of these cities, Cedarburg, was chosen for a more extensive study of concentration as a function of time throughout a 24-hour period. These results are presented in Figure 4.3. The concentration of PCBs in the raw waste water (influent) began to increase at 8:00 a.m., the beginning of the working day; the concentration rose from 0.54 ppb to a maximum of 3.1 ppb at 4:00 p.m. (1600 hours). The concentrations in the final effluent began increasing from 0.33 ppb at midnight (2400 hours) to a maximum of 0.77 ppb at 2:00 p.m. (1400 hours). Levels in both influent and effluent increased and decreased simultaneously throughout the day. Thus, in sampling to determine the extent to which waste effluents contribute to environmental contamination, it is extremely important to choose an appropriate time of day.

TABLE 4.9
PCB CONCENTRATIONS IN WISCONSIN TREATMENT PLANT EFFLUENTS

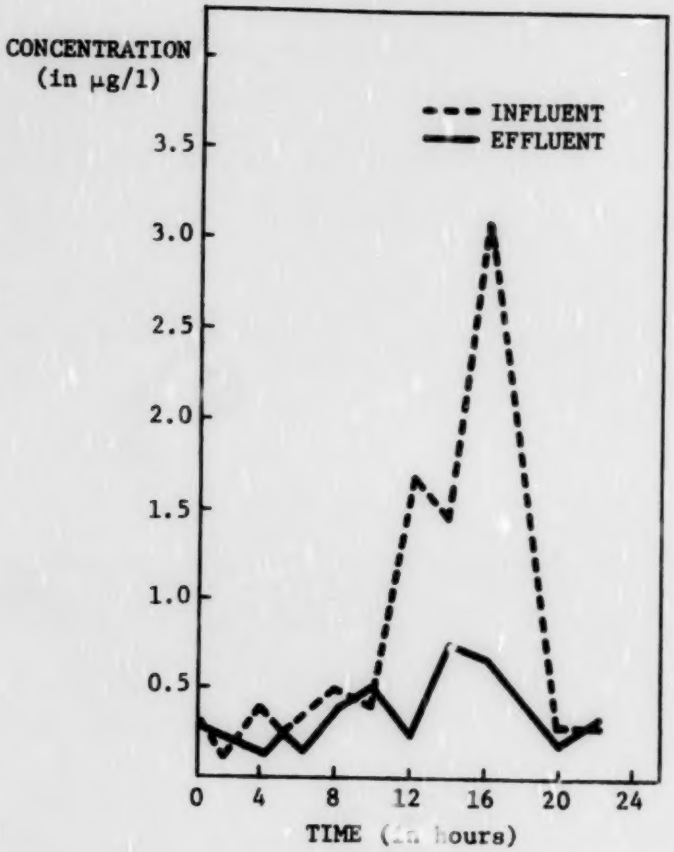
CITY	SAMPLING		PCB Concentrations* (µg/l)	Average Flow (mgd)	Estimated Mass Transport** (10^{-3} lb PCB/day)
	Date (1971)	Time			
Beaver Dam	1/20	6:30	<0.05	1.59	0.2
	2/19	6:30	<0.05	4.31	---
	3/22	6:30	<0.05	3.50	---
	10/6	6:30	<0.05	2.34	---
Port Washington	1/20	8:30	0.14	0.70	---
	2/19	8:30	0.12	1.27	---
	3/22	8:30	0.22	1.46	2.7
	10/6	8:30	0.19	1.80	---
Grafton	1/9	9:30	0.12	0.84	0.8
	2/19	9:30	0.13	1.00	1.1
	3/22	9:30	0.23	0.78	1.5
	10/6	9:30	0.07	0.84	---
Cedarburg	1/20	10:30	0.48	1.05	4.2
	2/19	10:30	0.28	1.17	2.7
	3/22	10:30	0.97	2.57	---
	10/6	10:30	0.91	1.95	15
	10/6	10:30	1.1	1.95	18
	10/6	10:30	1.0	1.95	16
Racine	1/20	8:30	0.72	16.45	---
	2/19	12:00	0.60	25.06	---
	3/22	12:00	0.76	23.01	---
	10/6	12:00	0.83	20.51	142
Burlington	1/20	9:30	0.14	1.74	---
	2/19	13:00	0.09	2.61	---
	3/22	13:00	0.08	2.50	1.7
	10/6	13:00	0.12	1.35	---
Lake Geneva	1/20	10:30	2.5	0.56	---
	2/19	14:00	2.2	0.66	---
	3/22	14:00	2.8	0.78	18
	10/6	14:00	2.4	0.54	---
Walworth	1/19	11:00	0.17	---	---
	2/20	14:30	0.21	---	---
	3/22	14:30	0.34	---	---
	10/6	14:30	0.18	---	---
Beloit	1/19	12:30	0.11	3.89	---
	2/20	16:00	0.07	11.75	---
	3/22	16:00	0.06	7.56	3.8
	10/6	16:00	0.14	4.42	5.2
Fort Atkinson	1/19	2:00	0.15	1.24	---
	2/20	18:00	0.07	2.48	---
	3/22	18:00	0.10	1.85	1.5
	10/6	18:00	0.08	1.30	---
Portage	5/20	10:00	42	0.79	---
	9/20	10:00	38	1.00	---
	10/6	10:00	32	0.78	---

* The chromatograms from all cities except for Portage most closely resembled the chromatogram of Aroclor 1254; the chromatogram from the Portage samples most closely resembled the chromatogram of Aroclor 1248.

** Mass transport estimates are based on concentrations observed during sampling multiplied by average daily flow.

Note: Mgd x 3,785 = cu m/day; lb x 0.454 = kg.

Source: Dube, D.J., G.D. Veith and G.F. Lee, 1974. "Polychlorinated Biphenyls in Treatment Plant Effluents", Journal Water Pollution Control Federation, 46(5): 966-972.



Source: Adopted from Dube, D. J., G. D. Veith and G. F. Lee, 1974. "Polychlorinated Biphenyls in Treatment Plant Effluents," Journal of Water Pollution Control Federation 46; 966-972.

FIGURE 4.3

HOURLY CONCENTRATIONS OF POLYCHLORINATED BIPHENYLS IN THE INFLUENT AND EFFLUENT FROM THE CEDARBURG, WISCONSIN, TREATMENT PLANT, APRIL 15, 1971

In the Cedarburg study, it was noted that the PCB concentration in the effluent was about 30 percent that of the influent and that the concentration in sludge was 1,000 times higher than that of the effluent. This treatment plant, therefore, removes 70 percent of the PCBs prior to discharge of the waste waters.

A laboratory study was initiated to ascertain the effectiveness of a secondary aerated biological oxidation system in removing high concentrations of PCBs from the effluent of primary treatment at the Jackson Pike (municipal sewage treatment) Plant in Columbus, Ohio (Choi et al., 1974). The laboratory system consisted of an aeration tank and a clarifier. The system was operated for 5 to 11 days in order to reach a steady state condition prior to introduction of PCB for a period of two to three days. Four to eight days of final operation followed. The results are presented in Table 4.10. PCB concentrations in feed, effluent, and sludge were 0.009,<0.001, and 0.07 ppm, respectively, prior to introduction of experimental levels. Concentration in sludge was 3600 times that in effluent on Day 3, the day of highest total concentrations. The PCB is probably dissolved in fats present in sludge, adsorbed at the surface of the suspended material in sludge or ingested by the microbial cells in sludge. It was concluded that a tertiary treatment system such as activated carbon might be necessary to further reduce the concentration in secondary system effluents.

TABLE 4.10 PCB CONCENTRATIONS IN SLUDGE AND EFFLUENT FROM AN EXPERIMENTAL BIOLOGICAL OXIDATION SYSTEM

Day after PCB added	Concentration in feed (ppm)	Concentration in sludge (ppm)	Concentration in effluent (ppm)
1	16.88	36.2	0.006
2	16.88	109.6	0.015
3	16.88	152.0	0.042
5	0	105.6	0.032
6	0	112.0	0.022
10	0	84.0	0.015

Source: Adapted from Choi, P.S.K., H. Nack and J.E. Flinn, 1974. "Distribution of Polychlorinated Biphenyls in an Aerated Biological Oxidation Wastewater Treatment System". Bulletin of Environmental Contamination and Toxicology, 11(1): 12-17.

The United States Environmental Protection Agency has proposed a final water quality criteria level for PCBs in fresh water of 1 ng/l (1 ppt) (Anonymous, 1975e), and it is believed that effluent standards will be revised shortly in accordance with this proposed criteria (Kopp, 1975).

The 1 ppt criteria is half the ambient level considered desirable by the EPA in 1972 (2 ng/l or 2 ppt) (U.S. Environmental Protection Agency, 1973a). Based on the 2 ppt level, effluent standards were proposed in 1973 requiring that the daily average PCB concentration in effluents must not exceed 280 μg/l or a total of 0.0294 kg per day (0.0648 pounds per day) into streams and 0.0245 kg/day (0.0540 pounds per day) into lakes (U.S. EPA, 1973b). Monsanto (1974d) argued against this standard as unrealistic from an environmental as well as a technological and economic point of view. PCBs, they claim, bioaccumulate, dissipate, and biodegrade at different rates and must, therefore, not be clumped together as of equal environment concern. With the exception of direct release near points of manufacture or use (which can be eliminated), the PCBs found in the environment are the pentachloro and higher isomers, even though 65 percent of all PCBs manufactured over the years contain four or fewer chlorine atoms.

Laboratory studies demonstrated that PCB isomers undergo degradation at rates dependent upon the number of chlorine atoms (Monsanto, 1972), and that lower-chlorinated isomers disappear through metabolism and/or excretion from the tissues of birds and mammals. Therefore, Monsanto argues, the lower-chlorinated species should be excluded when effluent standards are calculated. They also suggest that background levels already present in waterways be subtracted before a final effluent concentration is decided upon. The final concentration that Monsanto feels is reasonable is 1 pound (454 grams) in effluent for every 100,000 pounds (45,000 kilograms) produced (Monsanto, 1973a).

Industrial effluent standards (other than at the manufacturing plants) may be possible to meet now that many industries are no longer using PCBs in their products. Evidence that Monsanto's restriction of sales in 1970 may have had an immediate effect on some river systems was obtained by Veith (1972). These observations are summarized in Table 4.11. These data on rivers discharging into Lake Michigan show that PCB concentrations in two major tributaries decreased dramatically to below the detection limit seven months subsequent to the sales restriction.

In addition, the American National Standards Institute, in their 1974 guidelines for handling and disposal of PCB-containing askarels (American National Standards Institute, 1974), prohibits the disposal of waste askarel from capacitor and transformer factories down effluent drains and sewers and recommends incineration as the best method of disposal.

Since the highest concentration of PCBs from municipal sewage-treatment plants ends up in sludge, the manner in which sludge is disposed of is particularly important. A summary of data collected on

Table 4.11 CONCENTRATIONS OF PCB (μg/l as Aroclor 1254) IN SOME RIVER SYSTEMS

River	12/29/70	5/21/71	7/20/71	8/6/71
Peshtigo River	0.31	0.38	<0.01	<0.01
Oconto River	0.45	0.16	<0.01	<0.01
Pensawkee River	<0.01	<0.01	<0.01	<0.01
Big Suamico River	<0.01	<0.01	<0.01	<0.01
Fox River* (as Aroclor 1248)	0.18	0.26	0.16	0.15

* The Fox River is near a highly industrialized area.

Source: Adapted from G.D. Veith, 1972. "Recent Fluctuations of Chlorobiphenyls (PCBs) in the Green Bay, Wisconsin Region" Environmental Health Perspectives, Exp. 1: 51-54.

actual concentrations of PCBs in sewage sludges in the United States is presented in Table 4.12. Sewage sludge is disposed of by dumping it into the sea, depositing it in landfills, spreading it on land, or by incineration. In Britain, the high PCB concentrations detected in water from the Firth of Clyde was attributed to the routine dumping of crude sewage sludge from treatment plants in Glasgow and adjacent areas (Holden, 1970). In Britain, effluents from industrial sources are combined with those from domestic sources for purification. Many sludge samples so combined gave gas-liquid chromatograms similar to those of Aroclor 1254 and 1260 and ranged in concentration from <0.1 to 14 ppm (1 to 185 ppm in terms of dry material). Plankton samples were taken at Garroch Head (near the site of dumping) and at progressively further distances from the source and their PCB concentrations were measured. A marked gradation was observed from the Clyde (0.5 ppm) to the open waters of the Atlantic 400 miles from Scotland (0.041 ppm) (Williams and Holden, 1973).

Dumping at sea is therefore not the method of choice for disposal of sludge. Whether dumping on land or into sanitary landfills is any better is questionable. Leaching is theoretically possible when disposal sites are above permeable sand, gravel, or creviced bedrock formations. Toxic substances entering shale or clay, however, most likely do not migrate (Walker, 1973).

In a laboratory study (Tucker et al., 1975), distilled water was percolated through columns packed with several types of soil coated with Aroclor 1016 and the effluent waste was analyzed for PCBs. Breakthrough of PCBs into the effluent water appeared related to the clay content

Table 4.12 CONCENTRATION OF PCBs IN SEWAGE SLUDGES

Collection Site	Date	Aroclor Detected	Concentration (ng/g dry solids)	Sludge per day tons/day	Est. PCB Content lbs/day	Source
California						
Hyperion (Los Angeles)	12/70	1254	85[1] (78.5–92.1)	20,000[1]	3.2	Schmidt, et al., (13)
Barstow	7/21/71	1254	1,400	1.4	.004	EPA Unpublished data
Ohio						
Dayton (Miami River)		1254	105,000	47.9	10.1	EPA Unpublished data
Little Miami (Cincinnati)		1254	32,000	20.2	1.3	"
Mill Creek (Cincinnati)		1254	12,700	88.3	2.2	"
Lebanon (Turtle Creek)		1254	2,500	1.0	.005	"
Shayler Run		1254	3,200	---	---	"
Virginia						
Lorton		1254	1,200	---	---	"
Indiana						
Indianapolis		1254	3,800	126.1	1.03	"

[1] This number is based on outfall discharge and represents a relatively dilute sludge. The estimated PCB content in lbs/day is the important figure here.

Assumptions: Each million gallons of sewage contains about 1 ton of sludge. The daily output of sludge, then is 150,000,000 sewered population x 130 gal. sewage per day = 19,500,000,000 gallons per day and 19,500 tons of sludge per day nationwide.

Assuming 10 ppm of PCBs in sludge, the daily output would be 19,500 tons x 2000 lbs. = 39 million lbs. x 10 ppm = 390 lbs. per day, at 1 ppm, 39 lbs/day. These would be respectively 70 and 7 tons/year.

Source: Interdepartmental Task Force on PCBs, 1972. "Polychlorinated Biphenyls and the Environment", (Com-72-10419), Washington, D.C.

of the soil. As expected, soils containing higher percentages of clay retained the PCBs more effectively. But even in the worst case, less than 0.05 percent of the total Aroclor present was leached from the soil after a four-month exposure to a total of 100 liters of water. [The soil column height was 9 inches (23 centimeters); the diameter was 3 inches (8 centimeters)]. In addition, only the less-chlorinated, more easily degradable isomers were leached. From the results of this study, it would appear that leaching from landfills is not a significant source of environmental contamination and that landfills might be one possible method for sludge disposal. However, samples of surface runoff water from 5 landfills in Michigan showed concentrations of PCBs ranging from 0.04 to 0.30 micrograms/liter (ppb). Concentrations of PCBs in runoff water from four other Michigan landfills were below the 0.01 microgram/liter limit of detection (Hesse, 1975).

The method of choice for sludge disposal is incineration. PCBs in sewage sludge can be completely destroyed by this process (U.S. Environmental Protection Agency, 1972).

Nisbet and Sarofim (1972) have estimated that 300,000 tons (over 290,000 metric tons) of solid waste (including sludge) were deposited in dumps and landfills between 1930 and 1970. Analysis of stagnant water close to Swedish landfills revealed no detectable levels of PCBs where the limits of detection were 4 ppb (Lidgett and Vodder, 1970). At present, the approved method for disposal of scrap capacitors and the hardware from scrapped transformers is to seal them in containers and bury them in sanitary landfills (American National Standards Institute, 1974). This same method is used for any scraps of solid waste which are saturated with askarel. Monsanto believes that increased use of Aroclor 1016 for capacitor and transformer applications will significantly reduce the amounts of PCB isomers with six or more chlorine atoms released into the evnivronment from scrapped apparatus (Monsanto, 1972). Most of these PCBs will end up in landfills and the rest will be incinerated.

The high cost in investment casting wax has stimulated many foundaries to reclaim the wax after use. Even so, it is considered probable that large quantities of PCB-containing wax are disposed of, primarily in landfills. Wastes from spills and equipment clean-out are included with the unreclaimed wax and excess reclaimed wax in solid waste disposal (Versar, 1975a).

V. MEDIA DISTRIBUTION, TRANSFORMATION, AND TRANSPORT

A. SUMMARY

The ubiquitous polychlorinated biphenyls have apparently found their way into virtually all compartments of the environment. They were presumably released in highest concentrations prior to 1971, primarily to the air and water near urban, industrialized areas. However, data gathered subsequent to that date show significant levels of PCBs in air, fresh water, and marine samples from both industrialized and remote areas, suggesting that contamination is still occurring. Field studies have revealed PCB contamination in soil and laboratory studies indicate that certain types of soil readily adsorb PCBs and most likely contain them.

Atmospheric transport is the major pathway by which PCBs are carried to locations far from their point of entry into the environment. They are transported either as a vapor or adsorbed onto particulates and are deposited on land or into bodies of water by particle fallout and precipitation. Most of the PCBs reaching the hydrosphere are removed by particle scavenging, followed by sedimentation, and are only slowly released; small amounts remain dissolved and are subject to re-evaporation. Successive cycles of evaporation, adsorption, and deposition eventually carry the PCBs initially released on land to the coast and to their ultimate sink, the sediment of the oceanic floor.

B. ATMOSPHERE

Atmospheric transport plays a, if not the, major role in the worldwide dissemination of polychlorinated biphenyls (Södergren, 1972; Oloffs et al., 1972; Mackay and Wolkoff, 1973; Harvey and Steinhauer, 1974). The virtually universal distribution of PCBs in the global environment, including the Arctic and other areas protected from alternative routes of contamination, constitutes reasonable evidence for this phenomenon (Risebrough and deLappe, 1972).

The various pathways by which PCBs have entered the atmosphere over the past 40 years include incomplete incineration and burning of PCB-containing wastes in garbage dumps; vaporization from plasticizers, paints, and other coatings; vaporization from soil, sand, and other terrestiral reservoirs; evaporation and codistillation from natural bodies of water; and evaporation from their own surfaces when these have been exposed to the open air as in the case of accidental spillage, leaks, or wear and weathering of PCB-containing products.

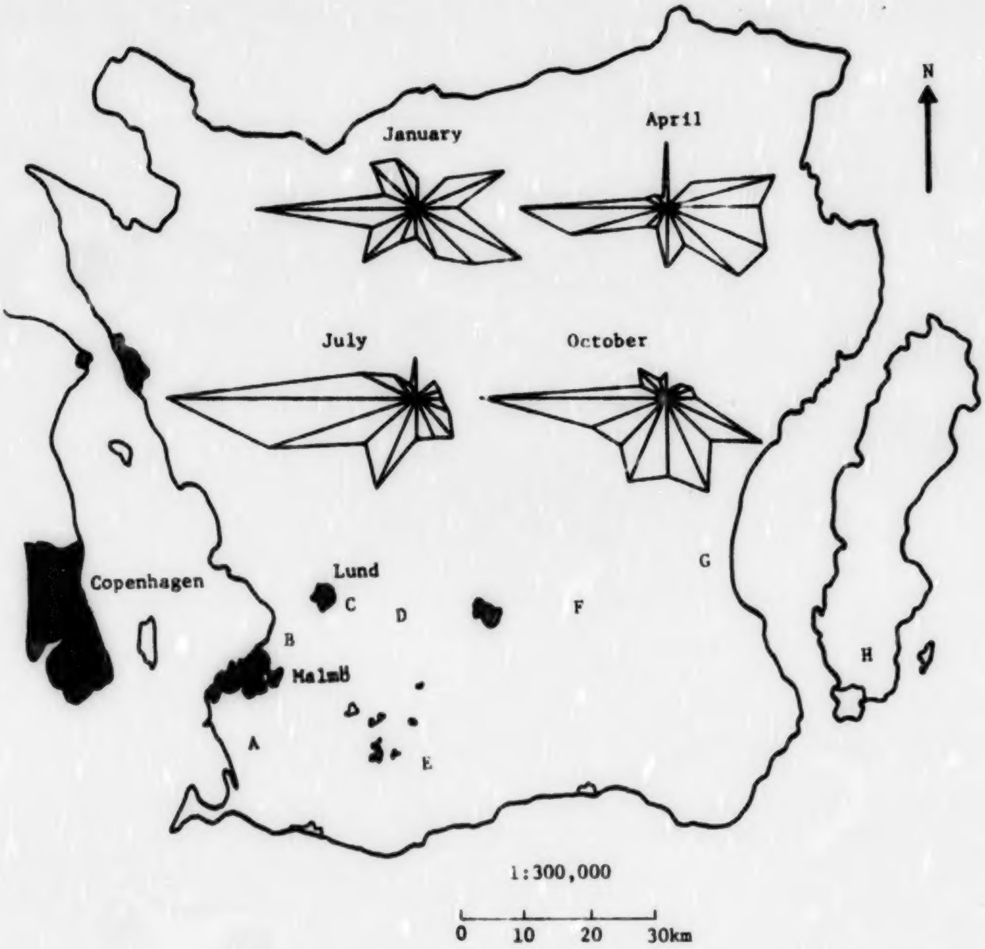
Nisbet and Sarofim (1972) claim that the contribution to atmospheric levels made by re-evaporation of the PCBs deposited into bodies of water will be negligible because of their low concentrations. But recent studies suggest that this may indeed be a significant route of contamination (see Section V.D.1). In addition, the failure to account for the bulk of the more than 2.8 billion kilograms (kg) of DDT dispersed in the environment since the 1940s, in conjunction with the observation that DDT vapor can be converted to PCBs by irradiation with ultraviolet light of the same wavelength present in sunlight in the lower atmosphere (Maugh, 1973), provides substance for speculation as to other possible sources of PCBs in the air. Evidence supporting the hypothesis that PCBs in the atmosphere may in fact be formed from DDT was provided in a recent study by Young and McDermott (1975) in which PCBs in dry aerial fallout were determined at various locations within the Los Angeles Basin. The highest levels (up to 1.7×10^{-6} g/square meter/day) occurred in the vicinity of the Montrose Chemical Company, which manufactures DDT. The second highest levels (up to 1.6×10^{-6} $g/m^2/day$) were found near the Kazarian landfill, the present disposal site for Montrose waste. By comparison, the Rolling Hills landfill, the disposal site for Montrose waste up until about 1972, showed levels ranging from 2.4×10^{-7} to 6.0×10^{-7} $g/m^2/day$. PCB levels at other stations throughout the Basin ranged from 7.8×10^{-8} to 9.3×10^{-7} $g/m^2/day$.

The period of greatest loss to the environment, including the atmosphere, presumably occurred during the decade 1960-1970 when PCBs were widely used in a variety of non-containable applications. Nisbet and Sarofim (1972), in their attempt to formulate a generalized description of the transport of PCBs through the North American environment, estimated that 1500 to 2500 tons a year of PCBs were being released directly into the atmosphere through vaporization from plasticizers (mainly Aroclor 1248-1260) and incomplete burning or incineration (Aroclor 1242). These figures were based on the 1970 sales by category of the Monsanto Company and reflected the authors' assumptions as to the useful service life of various PCB containing products and their logical modes of disposal. Continuing with their proposed model, it was estimated that the cumulative input of PCBs into the atmosphere from 1930-1970 amounted to about 3 x 10^4 tons. Due to chemical decomposition and metabolic transformation, a large proportion of the less-chlorinated isomers in the various Aroclor mixtures are expected to have been degraded. Consequently, about 2/3 (2 x 10^4 tons) of the amount originally lost to the air is believed to still remain in the environment, deposited on land, in the sea, or in fresh waters.

It can be expected that the highest concentrations of PCBs in the atmosphere will be found over industrialized urban areas. The PCBs may be found in the vapor phase, in the form of an aerosol, or adsorbed onto particulate matter. By analogy to DDT, Nisbet and Sarofim assumed that most airborne PCBs would be adsorbed onto particulates. Assuming the average rate of urban particulate production to be 2.67 x 10^7 tons per year, a rough estimate of 50 to 80 μg PCB/g of particulate in urban areas was calculated. An unpublished study by the U.S. Environmental Protection Agency of PCB levels on suspended particulates in four U.S. cities between 1968 and 1970 showed concentrations ranging from 27 to 230 μg PCBs per g of particulates (Interdepartmental Task Force on PCBs, 1972) with a mean concentration at 50 $\mu g/g$ of particulates. Assuming a particulate loading of 60 $\mu g/m^3$, this average amounts to 3 ng/m^3 PCBs. These values are consistent with the proposed model. In a more recent study (Kutz and Yang, 1975), samples of ambient air were collected from suburban locations in three U.S. cities (Miami, Florida; Jackson, Mississippi; and Fort Collins, Colorado) and analyzed for polychlorinated biphenyls by electron capture gas chromatography. Preliminary results for samples taken in April, May, and June of 1975 show that PCBs were present at all locations at an average concentration of 100 ng/m^3. The PCBs detected most closely resembled Aroclor 1254. No mention was made, however, as to what percentage of the observed PCBs was adsorbed onto particulates. Most of the PCBs adsorbed onto large particulates would be expected to be deposited on the land and nearby coastal waters within three days and would not be available for long-range transport.

The observation that PCBs must travel a long way by air in order to reach certain remote areas in which they have been found leads one to conclude that transport on small particulates or as a vapor must also take place to a significant extent as well.

Studies confirming the basic assumptions of the Nisbet and Sarofim calculations have been reported. The rate of input into the North American atmosphere estimated at 1.5 to 2.5 x 10^3 tons per year corresponds to a continent-wide mean rate of fallout of 60 to 100 m^2/year. In 1971, Persson reported a total fallout of 78 $\mu g/m^2$ i southern Sweden for a five month period in 1970 (Panel on Hazardous Trace Substances, 1972). This value is at least of a similar order of magnitude to that predicted by Nisbet and Sarofim. A second, rather detailed study on the monthly rate of fallout of PCBs in eight sites in Sweden during 1970-71 was performed by Södergren (1972). In this study, the amount of PCBs entering the areas investigated via airborne particulates and precipitation was determined. The locations of the fallout stations and the relative frequency of wind directions during several months of the year are shown in Figure 5.1. The most frequent direction is west to southwest. This means that the study area is subjected to airborne contaminants originating from the industrialized regions along the Swedish west coast as well as from those in Copenhagen and West Germany. Stations A, D, E, F, and G are located in agricultural districts; Station B is located in the city of Malmö close to a municipal refuse disposal plant; Station C is located in the city of Lund; and Station H is located in a forest district. The results of this study are summarized in Table 5.1. Values ranged from 550 to 10,510 ng/m^2/ month or from 7 to 126 µg/m^2 year, once again in the range predicted by Nisbet and Sarofim. The highest levels of PCBs were detected at Stations A and B, in the western part of the region. Despite the differences in type of location, PCB concentrations at these stations were very similar. Low to moderate levels of PCBs were observed at the more easterly stations C, E, F, G, and H. The unexpectedly high level at


N
January
April
July
October
Copenhagen
Lund
Malmö
A
B
C
D
E
F
G
H
1:300,000
0
10
20
30km

Source: Adopted from Södergren, A. 1972. Chlorinated Hydrocarbon Residues in Airborne Fallout , Nature 236, 395-397

FIGURE 5.1

THE LOCATION OF SAMPLING STATIONS FOR THE DETERMINATION OF PCB RESIDUES IN AIRBORNE FALLOUT IN SOUTHERN SWEDEN

Table 5.1 AVERAGE MONTHLY LEVELS OF PCB IN AIRBORNE FALLOUT COLLECTED IN SOUTH SWEDEN (ng m^{-2} $month^{-1}$)

Collecting Site*	Period of Collection	PCB
A	January-March 1971	10,510
B	January-March 1971	9,860
C	January-March 1971	1,740
D	January-March 1971	5,980
E	August-October 1969	910
	February-April 1970	4,460
	May-July 1970	1,590
	August-October 1970	550
	November-December 1970	1,800
	January-March 1971	850
F	January-March 1971	1,900
G	January-March 1971	2,190
H	January-March 1971	620

* The Symbols for the Collection Sites refer to Figure 5-1.

Source: Adapted from Södergren, A., 1972. Chlorinated Hydrocarbon Residue in Airborne Fallout. Nature 236: 395-397.

Station D was probably due to some unidentified local source. During the period February-April 1970, Station E experienced a significant increase in PCB fallout. This period was characterized by a high mean rate of precipitation. The evidence presented in this study provides some support for a model in which PCBs are carried through the air from industrialized regions to other areas in the path of the prevailing winds. This journey is occasionally shortened when the atmosphere is cleansed of particulates during precipitation.

Evidence that PCBs may reside in the atmosphere mainly as vapors was provided in a study by Bidleman and Olney (1974a). With the development of a new method for collection of polychlorinated biphenyl vapors (Bidleman and Olney, 1974b), it became possible to sample hundreds of cubic meters of air per day. Air was pulled at 0.4-0.8 m^3/min. through a glass-fibre filter and then through a plug of polyurethane foam. The filter is capable of removing 98 percent of particles having radii greater than 0.015 μm while PCB vapors are trapped on the polyurethane foam with an efficiency of greater than 90 percent. During the period from February to June 1973, PCB concentrations in the marine atmosphere of the Bermuda-Sargasso Sea area of the North Atlantic were measured. The samples were collected from a tower 20 meters high located at High Point, Bermuda. Marine air was also sampled from a tower 8 meters high on the bow of the R.V. Trident during a cruise from Bermuda to Narragansett, Rhode Island, in June 1973. Finally, local collections of PCBs were made on the University of Rhode Island campus and in downtown Providence. The results are presented in Table 5.2. Only a small amount (2 percent) of the PCBs detected were found on the glass-fibre filter, suggesting that, contrary to the prediction of Nisbet and Sarofim, adsorption onto particulates is not the major mode of transport of PCBs in the atmosphere. However, it is possible that PCBs volatilize from trapped particles, pass through the filter, and are subsequently collected by the polyurethane foam. The gas chromatograms of the PCBs in the atmosphere matched those of Aroclor 1242 and 1248, approximately 90 percent of which are tetrachloro or lower isomers. No concentration gradients were observed in going from the open sea towards Rhode Island although the urban concentrations were significantly higher (2.1-9.4 ng/m^3 in Rhode Island as compared to 0.21-1.6 ng/m^3 at sea). Since no wind direction, etc., was given, the explanation for the absence of a gradient is not obvious.

The question of whether or nor atmospheric gradients of PCBs exist from industrialized areas to the open sea was investigated by Harvey and Steinhauer (1974). Four stations over the western North Atlantic were sampled between January and June of 1973. The locations of sampling stations are shown in Figure 5.2 and the analytical results are presented in Table 5.3. The PCB concentrations were highest in Vineyard Sound located about 150-250 kilometers (km) from the Boston-Hartford -New York-New Jersey industrial complex. The concentrations over the Grand Banks, located over 2000 km from the north-

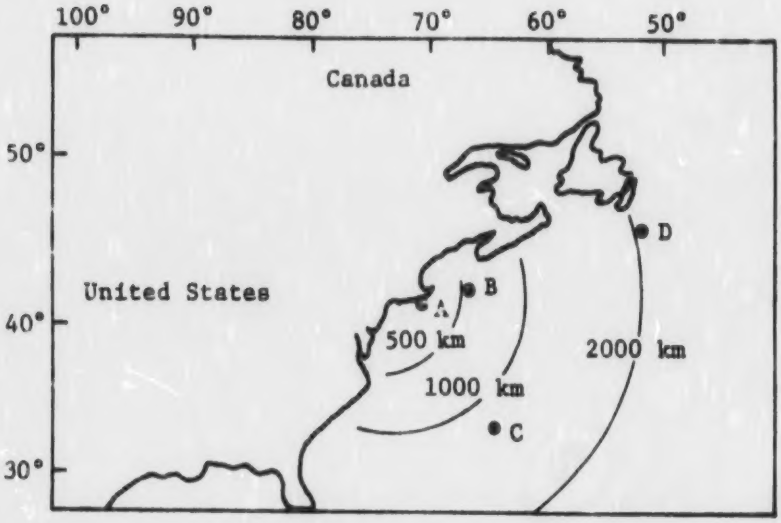
TABLE 5.2 CONCENTRATIONS OF POLYCHLORINATED BIPHENYLS IN MARINE AND CONTINENTAL AIR*

Sample	Collection dates (1973)	Location**	Volume of air (m^3)	PCB (ng/m^3)
1	2/12-2/13	Bermuda	1070	0.59
2	2/13-2/14	Bermuda	1320	0.30
3	2/15-2/16	Bermuda	918	0.65
4	2/16-2/18	Bermuda	1950	0.62
5	2/19-2/28	Bermuda	1740	0.55
6	2/29-3/9	Bermuda	732	0.52
7	4/8-4/11	Bermuda	1300	0.61
8	4/11-4/17	Bermuda	860	0.21
9	6/4-6/5	33°20'N, 65°14'W	300	1.6
10	6/5-6/6	34°39'N, 66°15'W	267	0.79
11	6/7-6/8	37°39'N, 68°12'W	402	-
12	6/8	38°48'N, 69°14'W	222	0.72
13	6/9	40°32'N, 70°20'W	196	0.83
14	1/18-1/19	U.R.I.	392	4.0
15	1/21-1/22	U.R.I.	1071	2.1
16	2/4-2/5	U.R.I.	744	5.8
17	5/8	Providence, R.I.	76	9.4

*The total retained by the glass-fiber filter and trapped on the polyurethane foam. Filter-retained values for the Bermuda samples were less than 2 percent of the total--,not determined; U.R.I., University of Rhode Island.

**Samples 9 through 13 were collected from the R.V. Trident while the ship was en route. The location marks the midpoint of the collection track.
Calculated as Aroclor 1242 or Aroclor 1248.

Source: Adopted from Bidleman, T. F., and C. E. Olney. 1974. Chlorinated Hydrocarbons in the Sargasso Sea, Atmosphere and Surface Water. Science 183: 516-518.


100°
90°
80°
70°
60°
50°
50°
40°
30°
Canada
United States
A
B
C
D
500 km
1000 km
2000 km

A = Vineyard Sound
B = Georges Bank
C = Bermuda
D = Grand Banks

Source: Adapted from Harvey, G. R., and W. G. Steinhauer. 1974. Atmospheric Transport of Polychlorobiphenyls to The North Atlantic. Atmospheric Environment 8: 772-782.

FIGURE 5.2

SAMPLING SITES OVER THE WESTERN NORTH ATLANTIC

TABLE 5.3 PCB CONCENTRATIONS OVER THE WESTERN NORTH ATLANTIC

Station	Date (1973)	Sample volume (m^3)	Wind direction	PCB ng m^{-3} (calc. as Aroclor 1254)
Bermuda	12 February	560	WNW	0.5
(32°20'N;64°40'W)	13 February	480	W	0.4
(32°20'N;64°40'W)	14 February	820	Variable	0.16
(32°20'N;64°40'W)	15 February	500	S	0.15
Georges Bank	10 April	105	NW	1.4
(41°40'N;67°30'W)	13 April	675	NW	0.82
(41°40'N;67°30'W)	15 April	660	NE	0.58
(41°40'N;67°30'W)	17 April	655	NW	0.61
(41°40'N;67°30'W)	19 April	640	SW	0.80
(41°40'N;67°30'W)	21 April	650	SW	1.60
Vineyard Sound	13 April	105	SW	3.9
(41°20'N;70°50'W)	30 April	224	SW	5.3
Grand Banks	25 June	780	SSW	0.05
(45°16'N;52°08'W)	26 June	960	SW	0.07
(45°16'N;52°08'W)	27 June	840	WSW	0.10
(45°16'N;52°08'W)	28 June	940	WSW	0.16
(45°16'N;52°08'W)	29 June	540	W	0.05

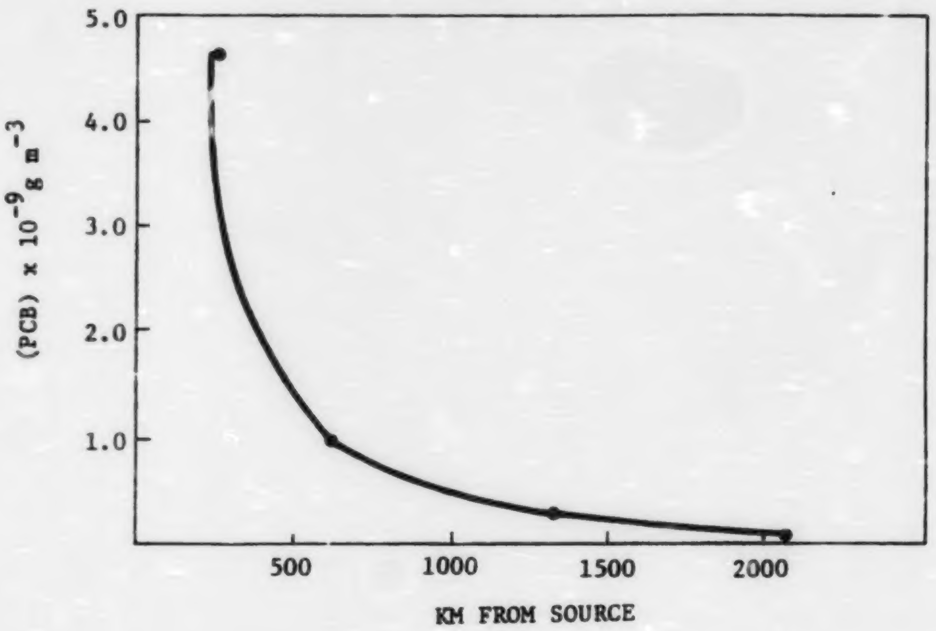
Source: Harvey, G. R., and W. G. Steinhauer. 1974. Atmospheric Transport of Polychlorobiphenyls to the North Atlantic. Atmospheric Environment 8: 772-782.

eastern industrial areas, were 100 times less than those over Vineyard Sound. The two middle stations showed intermediate levels of atmospheric PCBs. The PCB level reported over Bermuda agreed well with those observed by Bidleman and Olney in the previous study. When the average concentrations at each station were plotted against the average distance of the site from major industrial centers, the seaward decrease was seen to be exponential (Figure 5.3).

The method used for sample collection was one in which vapor phase PCBs and those adsorbed onto particulates could be differentiated. Once again, particulates were trapped on fiberglass filters, while PCB vapors were collected in silicone oil traps. Analyses of the fiberglass filters revealed PCB concentrations ranging from undetectable in the Grand Banks samples to 0.04 ng/m^3 over Vineyard Sound. Thus, only 1 percent or less of the total PCBs in the atmospheric samples were adsorbed onto particulates, providing further evidence for vapor phase transport.

C. HYDROSPHERE AND LITHOSPHERE

Nisbet and Sarofim (1972) estimated that roughly 6 x 10^4 tons of polychlorinated biphenyls were lost to the fresh and coastal waters of North America between 1930 and 1970. Metabolic transformation and chemical decomposition are expected to have degraded approximately 50 percent of this amount, leaving about 3 x 10^4 tons of PCB contamination in the North American hydrosphere. Of this remaining total, 2/3 or 2 x 10^4 tons were estimated to have been deposited into



Source: Harvey, G. R., and W. G. Steinhauer. 1974. Atmospheric Transport of Polychlorobiphenyls to The North Atlantic. Atmospheric Environment 8: 772-782.

FIGURE 5.3

RELATIONSHIP OF ATMOSPHERIC PCB AND DISTANCE FROM INDUSTRIAL SOURCES fresh-water systems via industrial and municipal waste-water effluents. Losses to the sea from such sources as river runoff, sediment transport, sewage-sludge and dredge-spoil dumping, accidental leaks from coastal industries, losses from ships, and deliberate dumping of industrial solid wastes presumably amounted to about 10^4 tons. An additional source of coastal contamination is aerial fallout and rainout. Of the 2×10^4 remaining tons of PCBs originally lost to the atmosphere, about 1/4, or 5×10^3 tons, is believed to have been deposited into the sea, mainly into the Atlantic Ocean. The total quantity of PCBs lost to North American coastal waters between 1930 and 1970 was, therefore, approximately 1.5×10^4 tons.

A recent study conducted by Young et al. (1975b) investigated inputs of chlorinated hydrocarbons into the Southern California Bight and established the importance of aerial fallout as a source of PCBs in the coastal waters of the Pacific. Dry aerial fallout was analyzed from 13 coastal and 5 island stations throughout the Bight during two 13-week periods. Samples consisted of duplicate 1-week collections. The fallout was collected on glass plates sprayed with a hexane-mineral oil mixture, a procedure developed by Dr. Vance McClure of The National Marine Fisheries Service, LaJolla, California. In addition, four other routes of input were investigated, including municipal waste-water effluents, industrial waste-water effluents, surface runoff, and antifouling paint from boat bottoms. The conclusions are presented in Table 5.4.

Table 5.4 ESTIMATED ANNUAL MASS EMISSION RATES OF POLYCHLORINATED BIPHENYLS TO THE SOUTHERN CALIFORNIA BIGHT (kg/yr)

Route	Year	1242 PCB	1254 PCB
Municipal wastewater	1974	4300	1100
Direct industrial	1973-74	--	60
Antifouling paints	1973	<1	<1
Surface runoff	1973	≤500	300
Aerial fallout	1973-74	≤1500*	1500
Total (Land)		4500-6000*	3000

*Assuming a 1 to 1 ratio between 1242 and 1254 PCB in aerial fallout.

Source: Young, D. R., D. J. McDermott, and T. C. Heesen. 1975. "Polychlorinated Biphenyls off Southern California." Paper presented at the International Conference on Environmental Sensing and Assessment, 14-19 September 1975, Las Vegas, Nevada.

It can be seen that the major source of PCBs is the marine discharge of municipal waste-water effluents. Surface runoff is of minor importance and direct industrial discharge is more or less insignificant. The second major source of PCBs in the Southern California Bight is aerial fallout. Analysis was conducted only for Aroclor 1254 and it was estimated that about 1500 kg/year of this PCB mixture enters the Bight by this route. However, since the concentration of Aroclor 1242 in surface runoff is of the same order of magnitude as that of Aroclor 1254, and since aerial fallout is a major contributor to surface runoff, it is estimated that aerial fallout of Aroclor 1242 is approximately equal to that of Aroclor 1254. In view of the severe air pollution problems in southern California, it is not surprising that aerial fallout has been found to play such a significant role in coastal contamination.

Some idea of the maximum possible levels of dissolved PCBs in the hydrosphere (excluding those adsorbed onto particulates and sediment, see Section V.D.3) can be obtained from solubility studies.

The solubilities of 21 PCB isomers in water have been tested (Wallnöffer *et al.*, 1973). With the exception of a few isomers, the more highly chlorinated the PCB, the lower its solubility in water. Values ranged from 5.8 ppm for 2-monochloro to 0.0072 ppm for 2,3,4,5,2',3',4',5'-octachloro biphenyl. Haque *et al.* (1974) studied the equilibrium between Aroclor 1254 and water and noted the final solubility. Equilibration was apparently complete after two months as no further increase in dissolved PCB was observed at six months. The final concentration was 56 ppb. From the relative intensities of the gas chromatogram peaks, it was concluded, in agreement with the study cited above, that the water solubilities of PCB isomers in general decrease with increasing chlorine content. It must be emphasized that, upon sampling natural waters for PCBs, sediment and suspected particulates will also be collected and total PCB concentrations can appear much higher. The observation of PCB concentrations as high as five times the solubility (275 ppb) in the Escambia River due to accidental leakage of hydraulic fluid from an air compressor was reported by Duke et al. (1970) (see Section IV.C.2).

Since municipal and industrial waste-water effluents contribute the major bulk of PCBs to fresh water systems (see Tables 4.7 and 4.8), one expects to find the highest concentration in rivers, streams, and lakes serving industrialized, urban areas. Nisbet and Sarofim adopted 0.5 parts per trillion (ppt) as a plausible background level for PCBs in unpolluted fresh water. They based this figure on the observation that water entering a Swedish waterworks contained 0.5 ppt. The relative lack of pollution in Scandinavian fresh waters was recently verified by Lunde (1975). Values ranging from 0.3 to 0.6 ppt were observed in the fresh water supply and tap water at Maridalsvennet, Oslo, and in the Göta and Nordre Rivers in Gothenburg. From scattered reports on PCB concentrations in North American fresh waters, Nisbet and Sarofim further estimated 5 ppt to be the mean concentration in the Great Lakes, 50 ppt in slightly polluted rivers (and also polluted bays), and 500 ppt in highly polluted industrialized rivers. The value for the Great Lakes was estimated from calculations based on the observed ΣDDT/PCB ratios in fish along with the known concentrations of DDT in the body of water considered. It was assumed that fish concentrate both of these chlorinated hydrocarbons in an identical manner. A gradient of ΣDDT/PCB in the direction of increasing PCB concentrations was noted in fish from four Great Lakes as follows: Superior (ratio = 2.4) < Huron (0.8) = Michigan (0.4-1) < Ontario (0.08-0.2). These increasing PCB levels from west to east are consistent with the relative industrialization of the areas. The PCB concentrations calculated for Lake Michigan ranged from 1 to 7.5 ppt; an actual value obtained in the summer of 1970 for this lake was 13 ppt (Interdepartmental Task Force on PCBs, 1972). Despite predictions that PCB concentrations in the Great Lakes would decrease as a result of Monsanto's restrictive sales policy, high levels in fish continue to be observed. Concentrations in lake trout have apparently increased from 12.5 ppm in 1972 to 19 ppm in 1973 to 23 ppm in 1974 (Anonymous, 1975d). Whether this increase is due to uptake of materials from past spills, negligent disposal practices (including low-temperature incineration followed by aerial transport), or use in unauthorized applications is uncertain. However, William Turney, Water Management Bureau Chief of the Michigan Department of Natural Resources, claims that if the U.S. Environmental Protection Agency does not take steps to halt the disposal of PCBs in the environment, he will recommend that PCBs be banned completely in Michigan (Mason, 1975). Values for slightly polluted rivers and polluted bays were based on the report of 40 to 70 ppt in Green Bay, Wisconsin, and 10 to 20 ppt in some rivers discharging into Lake Michigan (see Table 4.11) (Veith and Lee, 1971; Veith, 1972). The 500 ppt level for highly polluted industrialized rivers was based on determination of concentrations in the Milwaukee River, which ranged from 30 to 2,700 ppt (Veith and Lee, 1971). Another highly polluted river, the Great Miami River in Ohio, exhibited concentrations of PCBs ranging from undetectable to 15,800 ppt (the mean of 16 samples was 5,700 ppt) (Interdepartmental Task Force on PCBs, 1972), indicating that the Nisbet and Sarofim estimate may have been somewhat conservative.

A study by Veith and Lee (1971) concerning the fate of PCBs deposited in the Milwaukee River revealed that variations in the composition of the PCB mixtures occur as they travel downstream from their sources. A more rapid decrease in the concentrations of the less chlorinated isomers with respect to the more chlorinated isomers was observed. For example, the apparent Aroclor 1242 concentration in the lower river decreased from 2.07 μg/l at Estabrook Park to approximately 0.3 μg/l just below the North Avenue dam, a seven-fold reduction. In the same stretch of the river, the apparent concentration of Aroclor 1260 decreased from 0.1 to 0.05 μg/l, a two-fold reduction.

These observations provide support for the hypothesis that the less-chlorinated isomers are preferentially removed from the hydrosphere by vaporization, codistillation, and more rapid metabolic degradation.

A recent compilation of data gathered from monitoring activities of the Geologic Survey, U.S. Department of the Interior (Crump-Wiesner _et al_., 1974), testifies to the ubiquitous distribution of PCBs in the aquatic environment. The major drawback of this survey is that only one liter of water was collected at each site, imposing a lower limit of reproducible detection of 0.1 µg/liter. Thus, concentrations of less than 0.1 ppb were reported as "not detectable." Since Nisbet and Sarofim considered levels as low as 0.005 ppb to represent significant pollution, the present study must be considered incomplete. Nevertheless, the sites at which levels of 0.1 ppb or more were reported are representative of most regions of the country and constitute evidence for widespread contamination. The results are presented in Table 5.5. PCBs were recently discovered in Lake Anne, a 10-year-old man-made lake in Reston, Virginia (Martell _et al_., 1975). Concentrations ranged from 50-200 ppb, in the range approaching the Nisbet and Sarofim estimates for highly polluted rivers. Since there are no industrial or municipal discharges into Lake Anne and indeed little if any industry in Reston, the PCBs were assumed to originate from "diffuse sources associated with urban development and living." Aerial transport must also be considered as a possible route of input in this case.

Table 5.5 SUMMARY OF PCB RESIDUE DATA FOR SURFACE AND GROUND WATER, JANUARY 1971 - JUNE 1972

STATE	NO. SAMPLES	OCCUR-RENCES	CONCEN-TRATION, μg/LITER	MEDIAN CONCENTRATION, μg/LITER
Alaska	3	0	ND	ND
Arizona	8	0	ND	ND
Arkansas	32	0	ND	ND
California	161	2	0.1,0.1	ND
Colorado	32	1	0.3	ND
Connecticut	13	6	0.1-0.2	0.1
Hawaii	5	0	ND	ND
Iowa	24	0	ND	ND
Kansas	10	0	ND	ND
Kentucky	7	0	ND	ND
Louisiana	9	0	ND	ND
Maine	2	0	ND	ND
Maryland	6	1	0.1	ND
Massachusetts	5	1	0.2	ND
Michigan	2	0	ND	ND
Minnesota	3	2	0.1,0.3	ND
Mississippi	8	0	ND	ND
Missouri	21	0	ND	ND
Montana	47	0	ND	ND
Nebraska	44	0	ND	ND
New Jersey	11	3	0.1	0.1
New Mexico	36	0	ND	ND
New York	325	52	0.1-4.0	0.3
North Dakota	40	0	ND	ND
Oklahoma	19	0	ND	ND
Oregon	13	0	ND	ND
Pennsylvania	2	1	0.2	ND
Puerto Rico	7	1	0.1	ND
South Dakota	18	0	ND	ND
Texas	660	12	0.1-3.0	0.4
Virginia	4	1	0.1	ND
Washington	25	0	ND	ND
West Virginia	4	0	ND	ND
Wisconsin	3	0	ND	ND
Wyoming	18	0	ND	ND

NOTE: ND = Not Detected

Source: Crump-Wiesner, H. J., H. R. Feltz, and M. L. Yates. 1974. Pesticides in Water: A Study of the Distribution of Polychlorinated Biphenyls in the Aquatic Environment. Pesticide Monitoring Journal 8(3): 157-161.

Just as when dealing with atmospheric contamination, one must also be receptive to possible insidious sources of PCBs in the hydrosphere. Evidence was recently presented indicating the possible inadvertent manufacture of PCBs at a waste treatment plant. In November 1972, the failure of a municipal sewage treatment plant was reported. Reduction of biochemical oxygen demand was decreased by up to 30 percent of the reduction previously achieved. Half of the flow to the plant originated from a textile mill using at least 2 tons per week of biphenyl as a dye carrier for synthetic fibre. At the same time, the plant was subjected to significant concentrations of heavy metals from another industry. Between 150-190 kgs/day of chlorine gas was added to the system for influent odor control and effluent "disinfection." A PCB content of 18 ppm was subsequently noted on the filters of this plant (Gaffney, 1974).

It is generally accepted that the oceanic abyss represents an ultimate sink for PCB residues (Nisbet and Sarofim, 1972) with localized discharge and aerial fallout being the primary routes of contamination. The observation that approximately 1 ton per year of PCBs was being deposited into the Firth of Clyde in crude sewage sludge prompted an investigation of PCB levels in the surface and sub-surface waters of the Clyde Estuary (Holden, 1970). No PCB residues were detected in this study. However, subsequent analysis of plankton samples taken at a number of stations from the Firth of Clyde out to the International Ocean Weather Station India, 400 miles west of Scotland, revealed a gradient of PCB concentrations terminating at a level 12 times lower than that found in the polluted estuary (Williams and Holden, 1973).

Another study in which relative levels of PCB contamination in the ocean were inferred by comparison with the levels in plankton was reported by Harvey et al. (1974). In this study, PCB analyses were made on 53 plankton samples from both the North and South Atlantic. In both areas, the mean concentration was 200 µg/kg of wet weight and no discernable horizontal concentration gradients from coastal waters to the open sea were noted. This study is in conflict with that of Williams and Holden (1973) reported above. However, due to differences in collection procedure and the type of plankton, the two studies are not truly comparable.

The detection of significant quantities of PCBs in plankton is not surprising when it is remembered that plankton receive a large part of their nourishment from the surface layers of the sea. The surface microlayer contains a variety of surface-active substances such as fatty acids and fatty alcohols. These materials often form a visible film or slick; but the absence of such a film does not discount the likelihood of finding high concentrations of surface-active materials in the surface layers. The source of these compounds is the abundance of natural marine organic matter just below the surface. Surfactants are probably concentrated by convection currents, rising bubbles, and diffusion, with the more surface-active compounds displacing the less active ones. Many pollutants, especially the lipophilic variety such as chlorinated hydrocarbons, may be concentrated in this layer. Once concentrated, they are readily accessible to microorganisms, phytoplankton, and zooplankton residing at the surface. Thus, pollutants enter the food chain and are concentrated by the higher organisms in the hydrosphere.

The enrichment of the surface microlayer of Narragansett Bay, Rhode Island (an area basically free of industrial and municipal effluents and major ship traffic), with polychlorinated biphenyls was studied (Duce et al., 1972). Several surface microlayer samples, along with subsurface samples (20 centimeters [cm] below the surface) from each site, were collected and analyzed for polychlorinated biphenyls. The results of two samplings are presented in Table 5.6.

Sample 1 was collected from a heavy slick and showed an enrichment factor in the surface microlayer relative to the subsurface waters of ~28. Sample 2, from a less visible slick, showed an enrichment factor of ~9. Of cource, collection of the surface microlayer per se is impossible and the enrichment factors reported represented those of the first 100 to 150 micrometers (μm) of surface water. If the surface layer is assumed to be monomolecular, it should have a thickness of about 2×10^{-3} μm; if the film thickness is assumed (conservatively) to be five molecular layers of 1×10^{-2} μm and all of the chemical enrichment is concentrated in this film, the true concentration would be 1.5×10^{4} times the concentration in the first

Table 5.6 CONCENTRATION AND ENRICHMENT FACTORS OF POLYCHLORINATED BIPHENYLS (AS AROCLOR 1254) IN SURFACE MICROLAYER SAMPLES FROM NARRAGANSETT BAY, RHODE ISLAND

Sample 1			Sample 2		
Concentration (μg/liter)		Enrichment factor	Concentration (μg/liter)		Enrichment factor
Surface	Subsurface		Surface	Subsurface	
4.2±1.0	0.15 ± 0.04	28±10	0.45 ± 0.11	≤0.05	≥ 9

Source: Adopted from Duce, R. A., J. G. Quinn, C. E. Olney, S. R. Piotrowicz, B. J. Roy, and T. L. Wade. 1972. Enrichment of Heavy Metals and Organic Compounds in the Surface Microlayer of Narragansett Bay, Rhode Island. Science 176 (4031): 161-163.

150 μm actually sampled. In Sample 1, the true concentration would, therefore, be ~60 ppm or an enrichment factor of 4×10^5 for the film layer.

Other more recent studies have confirmed the importance of the surface microlayer in concentrating polychlorinated biphenyls. Bidleman and Olney (1974a) sampled both the surface (first 150 μm) and subsurface (30 cm below the surface) waters of the Sargasso Sea in a range of 80 to 320 kilometers south of Bermuda. Their results are presented in Table 5.7. While the predominant gas chromatographic patterns of atmospheric samples taken near Bermuda resembled Aroclor 1242 or 1248 (see Section V.B), the most abundant mixtures in the water were Aroclor 1254 and 1260. This finding is in agreement with results of fresh water studies and suggests that vaporization, codistillation, and metabolic degradation of the lower isomers result in the concentration of higher isomers in the hydrosphere. Once again, an enrichment of the surface microlayer was noted. Except for one sample, that taken on 11 April 1973 when excessive windborne dust was carried to sea, the enrichment factors (average = 5.2) were lower than those noted previously by Duce et al. (1972) in Rhode Island waters. This might be expected since the Sargasso Sea area is one of high evaporation and low rainfall and, once again, stresses the importance of atmospheric transport of PCBs to the sea.

In another study conducted from June through October of 1972 (Harvey et al., 1973), PCB concentrations in the open ocean water of

Table 5.7 POLYCHLORINATED BIPHENYLS (AS AROCLOR 1260) IN SARGASSO SURFACE MICROLAYER (SM) AND SUBSURFACE WATER (SS)

Collection date (1973)	Location	Sample	PCB* (ng/liter)	Enrichment factor
4/9	29°56'N,64°40'W	SM	11.2	3.1
		SS	3.6	
4/10	30°45'N,66°50'W	SM	4.9	5.4
		SS	<0.9	
4/10	30°34'N,66°59'W	SM	8.3	8.3
		SS	1.0	
4/11	28°53'N,65°07'W	SM	42.6**, 19.3	47.3
		SS	<0.9**, <0.9	21.4
4/12	29°56'N,63°00'W	SM	3.8	4.2
		SS	<0.9	
4/13	30°00'N,64°30'W	SM	5.6	3.5
		SS	1.6	
4/16	31°34'N,63°49'W	SM	5.0	2.8
		SS	1.8	
4/17	31°38'N,63°57'W	SM	8.4	9.3
		SS	<0.9	

***Blank value was 0.9 and was subtracted in calculating the above results.**

**Sample taken in a *Sargassum* windrow.

Source: Adopted from Bidleman, T. F., and C. E. Olney. 1974. Chlorinated Hydrocarbons in the Sargasso Sea, Atmosphere and Surface Water. *Science* 183: 516-518.

both the eastern and western North Atlantic were determined. The results are presented in Table 5.8.

The widespread distribution of PCBs (mainly as Aroclor 1254) once again is suggestive of atmospheric transport. Radically different concentrations at points fairly close together were observed and were attributed to seaslicks, localized discharge from ships, and localized rainfall. Just as was the case with plankton (Harvey *et al.*, 1974a), no concentration gradients were noted from coastal waters to the open sea. PCB concentrations decrease with depth, but they are still detectable at levels greater than 1 ppt, 3000 meters below the surface. Although a wide range of concentrations exists, the average concentrations in the northern North Atlantic surface waters and subsurface waters (200 m below the surface) are 35 ppt and 10 ppt, respectively. The surface waters of the Sargasso Sea had slightly lower surface concentrations (average = 27 ppt) than those in other parts of the North Atlantic but were 10 to 20 times higher than those reported by Bidleman and Olney (1974) in April of 1973.

Continued monitoring of North Atlantic surface waters by Harvey *et al.* (1974b) revealed that PCB levels had declined approximately 40-fold since the 1972 survey (Harvey *et al.*, 1973). Levels of 0.8 ng/l were reported in samples from the Sargasso Sea to the New York Bight and the New England Continental Shelf during February of 1974. These values were in good agreement with those of Bidleman and Olney (average = 1 ng/l).

Table 5.8 CONCENTRATIONS OF PCBs IN NORTH ATLANTIC OCEAN WATER
(the limit of detection was 1 x 10^{-9} g/liter for a 19-liter sample)

STATION	POSITION		DATE (1972)	DEPTH (m)	PCB CONCENTRATION* (X 10^{-9} g/LITER)
	NORTH	WEST			
1	52° 55'	35° 08'	6/30	0	150
2	44° 00'	30° 36'	7/3	0; 200	35; 10
3	40° 33'	29° 16'	7/5	0; 200	4; 7
4	36° 11'	25° 33'	7/7	0; 200	11; 3
5	34° 02'	22° 50'	7/9	0; 200	30; 6
6	35° 00'	18° 59'	7/11	0; 200	14; 5
7	34° 47°	14° 57'	7/13	0; 200	67; 39
8	38° 20'	11° 23'	7/15	0; 200	19; 2
9	38° 23'	11° 11'	7/22	0; 200	41; 13
10	38° 19'	19° 28'	7/23	0	77
11	41° 09'	20° 46'	7/24	0	< 1
12	43° 57'	22° 13'	7/25	0	52
13	43° 20'	21° 57'	7/27	0	47
14	43° 16'	21° 34'	7/29	100; 3000	45; > 1†
15	46° 31'	21° 43'	7/30	0	10
16	52° 31'	19° 52'	8/1	0; 100	45; 8
17	52° 35'	19° 53'	8/2	1500	> 1†
18	55° 41'	15° 02'	8/4	0	3
19	57° 22'	12° 01'	8/5	200	97
20	60° 04'	06° 02'	8/6	200	42
21	60° 09'	05° 36'	8/7	0	82
22	60° 29'	04° 43'	8/7	0	23
23	63° 03'	02° 22'	8/8	0; 200	21; 7
24	41° 32'	70° 40'	10/2	0	30
25	39° 40'	70° 03'	9/21	0	29
26	37° 12'	68° 54'	9/22	0	36
27	34° 32'	67° 01'	9/23	0	12
28	35° 22'	67° 36'	9/24	1000	1
29	35° 17'	68° 28'	9/24	0	2
30	35° 56'	66° 34'	9/25	0	5
31	36° 05'	67° 27'	9/26	0	11
32	36° 24'	68° 24'	9/27	0	22
33	35° 37'	67° 49'	9/27	0	9
34	34° 26'	66° 22'	9/28	0	12
35	33° 41'	65° 44'	9/28	0	15
36	28° 42'	58° 39'	10/3	0	26
37	26° 50'	55° 38'	10/5	0	36
38	25° 56'	54° 15'	10/6	0	27
39	26° 58'	53° 57'	10/7	0	42
40	28° 26'	53° 55'	10/8	0	88
41	31° 13'	53° 49'	10/9	0	68

*The closest matching commercial mixture in all cases was that containing 54 percent chlorine. Thus, the commercially available Aroclor 1254 (Monsanto) was used as the standard. Procedural blanks ranged from 0 to 3 ng/liter and were subtracted from the tabulated concentrations: DDT and its metabolites, if present, were present at concentrations less than 1 ng/liter.

Source: Harvey, G. R., W. G. Steinhauer, and J. M. Teal. 1973. Polychlorobiphenyls in North Atlantic Ocean Water. Science 180:643-644.

The volume of the upper 200 m of the North Atlantic is 10^{18} liters. If the average PCB concentration in that volume during 1972 was 2×10^{-8} g/liter (20 ppt), then a total of approximately 2×10^{4} tons of PCBs were present in the water at that time. This value is in excellent agreement with the value of 1.5×10^{4} tons predicted by Nisbet and Sarofim (1972). However, to account for the 40-fold decrease in concentration observed between 1972 and 1973, the data require that almost 2×10^{4} tons of PCBs were lost from the upper 200 m in less than one year (Harvey et al., 1974b). Longhurst and Radford (1975) derived a mean residence time for PCB in seawater in the North Atlantic based on a standing stock of 2×10^{4} tons and the 40-fold decline which reportedly took place in the year 1972 to 1973.

The model used for these calculations simulated the loss process on a daily basis by reducing the standing stock (S) by a constant (S/r). The value of the mean residence time, r, was calculated so as to reduce S ($=2 \times 10^{4}$ tons) by 97.5 percent (40-fold) in 365 days; r was calculated to be just under 100 days. In order for this system to sustain the reported standing stock of 2×10^{4} tons, the annual input to the waters must have been of the order of 7.3×10^{4} tons. This figure seems improbable since it necessitates that the entire world production of PCBs was continuously dumped into the North Atlantic (annual world production figures between 1967 and 1970 averaged 7.27×10^{4} tons). Longhurst and Radford suggested that either the analytical results are not correct, with the 1971 to 1972 data (21 to

41 μg/1) being too high and the 1973 to 1974 data (0.8 to 2.0 μg/1) being too low or the extrapolation from individually correct data to a standing stock for the entire North Atlantic being unfounded. Harvey and Steinhauer (1975) replied to this argument by reaffirming the validity of their analytical results but admitting that their extrapolation to the entire North Atlantic was not justified. The large decrease in concentration was observed in the North American basin between 1972 and 1974 and most likely reflected changes in the North American PCB input. Since continuous monitoring data for the same period is not available for other areas, it is not possible to draw any conclusions regarding trends in concentration.

According to Nisbet and Sarofim, approximately 1.5 x 10^4 tons of PCBs were distributed over terrestrial North America between 1930 and 1970 (Nisbet and Sarofim, 1972). However, relatively little data on concentrations of PCB residues in soil are available. In one study (Carey et al., 1973), soil and crops from 400 sites in 12 states comprising the corn belt were analyzed for levels of organochlorine pesticide residues (including PCBs) during 1970. PCB residues were apparently not detectable in the soil itself as no data was given. However, Aroclor 1232 and 1242 were identified in the crops. The PCBs were found in cornstalk and hay samples from six of the 12 states studied. Concentrations in 10 cornstalk samples (6.9 percent of those tested) ranged from 0.53 to 6.25 ppm (average, 2.8); concentrations in three samples of mixed hay (27.3 percent of those tested) ranged from 0.8 to

2.94 ppm (average, 0.57). It was concluded that the PCBs entered the crops through translocation from the soil and that the soil could, therefore, be assumed to be contaminated.

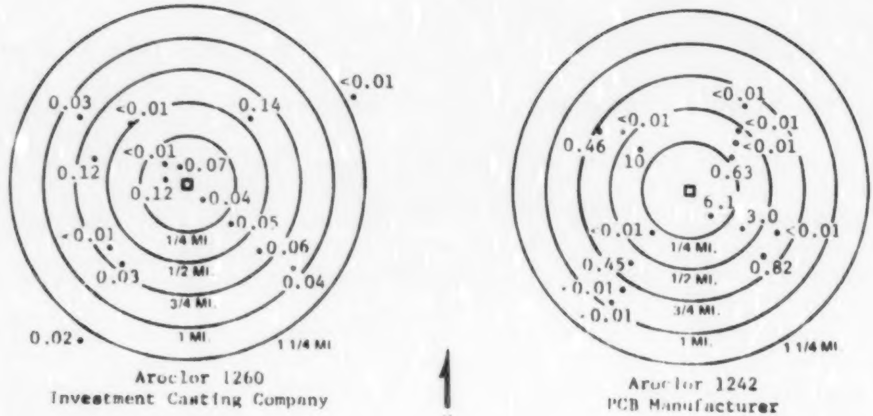
A comprehensive program for monitoring levels of pesticide residues in soils of the United States (The National Soils Monitoring Program) was initiated in 1969 as part of the National Pesticide Monitoring Program. One small segment of this program monitors five urban areas each year and includes analyses for PCBs (Ruopp and DeCarlo, 1975). PCBs were detected in three of the five cities sampled in each year for which data are available (1971 to 1973). Of the 22 positive samples, 17 were below 1 ppm. Pittsfield, Massachusetts, the home of a large transformer plant which uses PCBs, was sampled during the 1973 survey. No PCB residues were detected in any of six sites located within a one-mile radius of the plant. In another study, conducted for the Office of Toxic Substances, soils were sampled near a plant in Illinois using PCBs in the manufacture of investment casting wax (Ruopp and DeCarlo, 1975). Samples taken within a quarter-mile radius around the plant ranged in value from 0.77 to 5.2 ppm total PCB. The PCBs were identified as Aroclor 1260 and decachlorobiphenyl. Levels up to 1.8 ppm Aroclor 1260 were detected up to one and one-quarter miles from the plant.

In March of 1975, sites were sampled in the vicinity of an investment casting company in Michigan and a PCB manufacturer in Illinois (Ruopp and DeCarlo, 1975). Surface soil samples were collected at one-quarter mile intervals up to one mile from each plant in all directions. PCBs were detected at both locations. Aroclors 1242 and 1260 as well as decachlorobiphenyls were detected near the PCB manufacturers but only Aroclor 1260 was detected near the investment casting plant. Total concentrations ranged from 0.001 ppm to over 20 ppm. Values were highest near the plant sites and, in general, decreased with increasing distance from the site. The actual concentrations at every sampling site for each of the three plants where soil contamination was observed are presented in Figure 5.4.

D. TRANSPORT AT INTERFACES

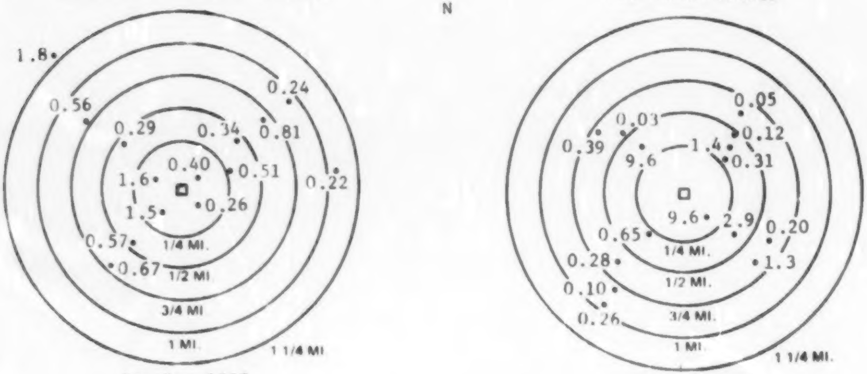
1. Air/Water Interface (including precipitation)

"From a pollution standpoint, the air-sea interface is perhaps one of the most important regions of the marine environment" (Duce et al., 1972). In the case of PCBs, ample evidence exists to support this statement. The observation of significant concentrations of PCBs in the marine atmosphere, far removed from urban industrialized areas, suggests that atmospheric transport represents the major route of PCBs to the sea (Harvey and Steinhauer, 1974; Bidleman and Olney, 1974a; see Section V.B). It follows logically that the surface microlayer would be the first compartment of the hydrosphere to receive the majority of PCBs deposited into the ocean. Surface-active agents, including a high concentration of lipids, which comprise the surface slick are receptive to lipophilic compounds such as the chlorinated hydrocarbons and thus tend to concentrate and


<0.01
0.03
<0.01
0.14
<0.01
0.07
0.12
0.12
0.04
0.05
<0.01
0.06
0.03
0.04
0.02
1/4 MI.
1/2 MI.
3/4 MI.
1 MI.
1 1/4 MI.
N
<0.01
<0.01
<0.01
0.46
<0.01
10
0.63
6.1
3.0
<0.01
<0.01
0.45
0.82
<0.01
<0.01

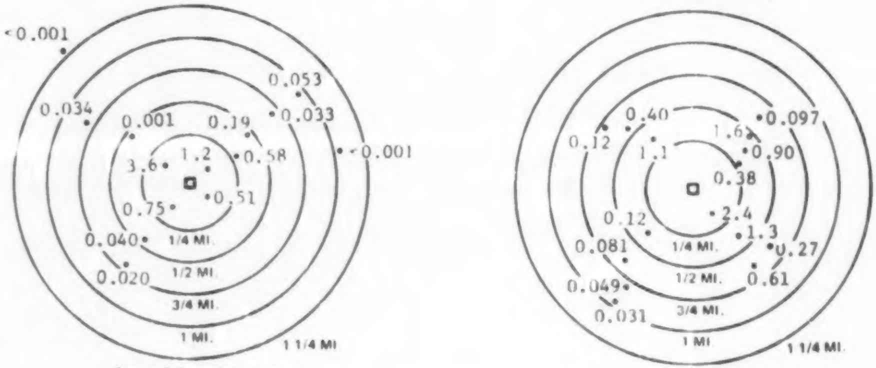
Aroclor 1260
Investment Casting Company

Aroclor 1242
PCB Manufacturer


1.8
0.24
0.56
0.29
0.34
0.81
0.40
0.51
1.6
0.22
0.26
1.5
0.57
0.67
1/4 MI.
1/2 MI.
3/4 MI.
1 MI.
1 1/4 MI.
0.05
0.03
0.12
0.39
1.4
9.6
0.31
9.6
2.9
0.20
0.65
0.28
1.3
0.10
0.26

Aroclor 1260
Investment Casting Wax Manufacturer

Aroclor 1260
PCB Manufacturer


<0.001
0.053
0.034
0.001
0.19
0.033
1.2
0.58
<0.001
3.6
0.51
0.75
0.040
0.020
1/4 MI.
1/2 MI.
3/4 MI.
1 MI.
1 1/4 MI.
0.40
0.097
0.12
1.6
1.1
0.90
0.38
0.12
2.4
1.3
0.081
0.27
0.61
0.049
0.031

decachlorobiphenyl
Investment Casting Wax Manufacturer

decachlorobiphenyl
PCB Manufacturer

Source: Ruopp, D.J. and V.J. DeCarlo. 1975. Unpublished material re: "Environmental Levels of PCBs."

Figure 5.4 CONCENTRATION OF PCBs IN SOIL WITH DISTANCE
(ppm)

stabilize them. The highest concentrations of dissolved PCBs would, therefore, be expected to reside in the surface microlayer and indeed have been found to do so (Bidleman and Olney, 1974a; Duce et al., 1972; Harvey et al., 1973; see Section V.C).

The microorganisms and plankton that live in the first 100 meters below the surface subsequently ingest and/or absorb the PCBs dissolved in this surface microlayer and, by this route, the PCBs enter the marine food chain. The high concentrations of PCBs in plankton from waters that themselves contained undetectable levels of PCBs (Williams and Holden, 1973) testify to this occurrence.

Bidleman and Olney (1974a) estimated the residence time of PCBs in the atmosphere over the Sargasso Sea from the mean concentrations in the air ($5\text{x}10^{-10}$ g/m^3; Table 5.2 samples 1-8) and subsurface waters ($1.1\text{x}10^{-6}$ g/m^3*) using the following assumptions:

> (i) except for the surface microlayer, PCBs are uniformly distributed in the top 100 m and have a resident time there of 4 years, (ii) the atmospheric concentration is constant up to the tropopause and zero above, (iii) the major source of PCB input is the atmosphere.

Using the mean air and water concentrations given above, the quantity of PCBs in a column of air 1 m^2 extending up to the tropopause, a distance equivalent to 6.3 kilometers after correcting to standard conditions (0°C, 760 mm pressure), is ($6.3\text{x}10^3$ m^3) ($5\text{x}10^{-10}$

---

*This value is obtained by averaging the values on Table 5.7 by two different methods.
a) assume <0.9 = 0.9; average = 1.4 ng/l = $1.4\text{x}10^{-6}$ g/m^3
b) assume <0.9 = 0.0; average = 0.89 ng/l = $0.89\text{x}10^{-6}$ g/m^3
The average of these two results is $1.1\text{x}10^{-6}$ g/m^3.

g/m^3) or 3.15×10^{-6} grams; that in a column of water 1 m^2 extending down to 100 m is (1×10^2 m^3) (1.1×10^{-6} g/m^3) or 1.1×10^{-4} g.

Let the residence time in air, Ta, equal N/(dN/dt) where N is the quantity of PCB in the air (3.15×10^{-6} g) and dN/dt is the rate of loss from air into water. If the residence time in water, Tω, is 4 years

then d(PCB)/dt = 1.1×10^{-4} g/4 years or 2.8×10^{-5} g/year

Ta then equals 3.15×10^{-6} g/2.8×10^{-5} g/year or 0.11 years or 40 days.

Harvey et al. (1973) reported PCB concentrations in Sargasso Sea surface waters 10 to 20 times higher. If these concentrations are correct, the residence time would be an order of magnitude shorter.

Some studies have been reported in which an attempt was made to detect the presence of PCBs in precipitation. Bevenue et al. (1972) analyzed rainwater in Hawaii for the presence of organochlorine pesticide residue. While some pesticide residues were present, under the conditions of this study, no PCBs were detected. The pesticides observed, however, could be easily detected at the 1 ppt level; PCBs on the other hand would have had to be present in concentrations of 20-40 ppt for minimum detection. One therefore cannot conclude that PCBs are absent from Hawaiian rainwater. Tarrant and Tatton (1968) examined rainwater collected continuously at seven widely distributed sites in the British Isles chosen so as to represent a variety of conditions and locations. Small amounts of PCBs were detected in all the samples but were not quantified.

Samples of snow were collected at seven locations in Wisconsin, allowed to melt in the laboratory, and analyzed for PCBs. Three samples (Green Bay, Grafton, and Kewaskum) were below the 0.01 ppb level of detection. However, samples from Racine, Kenosha, Madison, and Milwaukee displayed 0.17, 0.22, 0.24, and 0.20 ppb PCB, respectively (Kleinert, 1976).

Peel (1975) took advantage of the unique characteristics of Antarctica to study the role played by precipitation in the transport of PCBs. The absolute lack of any nearby source of emission along with the lessened probabilities of interference by other, more dominant organochlorine compounds make Antarctic snow an ideal form of precipitation to study. In addition, the sub-zero temperatures and negligible biological activity in the snow minimize the possibilities of chemical alteration or diffusion once precipitation has been deposited. Ten snow samples laid down between 1965 and 1969, 360 and 400 km from the coast, were collected and analyzed. Low levels ($5x10^{-14}$ g/g) of PCBs were found in the snow samples. These results agree with resident animal data from the area which show Σ DDT/PCB ratios much larger than those found north of the Antarctic convergence. However, since Antarctica is about as far as one can get from urban industrialized areas, the fact that PCBs can be detected at all in snow samples constitutes reasonable evidence for airborne precipitation mediated PCB transport.

Although Nisbet and Sarofim (1972) put little weight on transport of PCBs from the surface of bodies of water back to the atmosphere, evidence exists that such reentry does in fact occur. A laboratory study was reported (Oloffs, et al., 1972) in which the fate of PCBs (Aroclor 1260) in three natural water samples was demonstrated. The sources were (a) the Fraser River at New Westminster in British Columbia, 10 miles east of Vancouver, (b) two miles above the mouth of the Nicomekl River at a point 20 miles southeast of Vancouver and (c) the shoreline of the Georgia Strait, 15 miles north of Vancouver. To 150 milliliters (ml) of each water sample in a 500-ml Erlenmeyer flask, 0.1 ppm of Aroclor 1260 was added. The flasks were plugged with glass wool, swirled, and allowed to stand for 12 weeks with swirling once per day. The results are presented in Table 5.9.

PCBs concentrations were seen to decrease in the samples of natural water even at temperatures as low as 7°C. However, the peak heights in the gas chromatograms did not change relative to one another and the overall gas chromatographic pattern remained identical to that of Aroclor 1260. No new peaks were observed nor were any metabolites detected. Thus, whatever the fate of the Aroclor 1260 mixture was, all of its isomers behaved in a similar manner. Significant amounts, up to 6.2 percent, of the added PCB were detected in the glass wool indicating that evaporation had taken place. Since the initial concentration of Aroclor 1260 was greater than its solubility, it was postulated that the excess PCBs accumulated at the

Table 5.9 THE FATE OF 0.1 ppm POLYCHLORINATED BIPHENYL (AROCLOR 1260) IN 150 ml WATER SAMPLES FROM THE FRASER RIVER, THE NICOMEKL RIVER, AND GEORGIA STRAIT HELD IN THE LABORATORY FOR 12 WEEKS AT THE GIVEN TEMPERATURE

Recovery, %

	Fraser River (7°C)			Nicomekl River (16°C)			Georgia Strait		
Time (weeks)	Water	Glass Wool	Lost	Water	Glass Wool	Lost	Water	Glass Wool	Lost
0	95.6	0	4.4	96.2	0	3.8	93.5	0	6.5
6	60.1	1.8	38.1	73.8	1.4	24.8	70.7	1.3	28.0
6	60.9	4.5	34.6	74.5	1.6	23.9	40.7	6.2	53.1
12	64.1	1.2	34.7	33.0	1.1	65.9	37.7	2.4	59.9
12	74.7	5.6	19.7	56.7	1.1	42.2	38.7	0.8	60.5

Source: Adapted from Oloffs, P. C., L. J. Albright, and S. Y. Szeto. 1972. Fate and Behavior of Five Chlorinated Hydrocarbons in Three Natural Waters. *Canadian Journal of Microbiology* 16: 1393-1398.

water/air interface and subsequently evaporated. The PCBs unaccounted for (see "% lost" column, Table 5.9) were assumed to have been lost from the glass wool into the atmosphere. The authors neglected to take into consideration the fact that PCBs tend to adsorb tenaciously to glass surfaces (see Section V.D.3) and were probably lost, to some extent, by this route. Nevertheless, their presence on the glass wool is ample evidence for the plausibility of re-evaporation from natural waters contributing to atmospheric contamination under certain conditions. A similar study using the chlorinated hydrocarbon pesticide chlordane revealed that the presence of materials that promote the even distribution of these residues in natural waters (e.g., detergents) will minimize this accumulation at the surface and, in turn, their evaporation. Because of similarities in properties, such a phenomenon is applicable to PCBs as well and they therefore should be expected to behave differently in sewage outfalls or in bodies of water serving industrialized areas than in other natural waters.

When considering the evaporation of PCBs from water, one tends to assume that due to their high molecular weight and low vapor pressure, evaporation should be slow. A factor that is overlooked, however, is their high activity coefficients in water, which, when multiplied by the molecular concentration, yield the active mass or actual number of gram molecular weights per liter in solution or in gaseous form. This results in unexpectedly high equilibrium vapor partial pressure and consequently high rates of evaporation. An attempt was made to quantify the rates of evaporation of low-solubility contaminants such as PCBs from water bodies to the atmosphere (Macday and Walkoff, 1973). The results are given in Table 5.10.

The assumptions made in calculating these data are as follows:

(a) The contaminant concentration used is that of dissolved PCBs and excludes those in suspended, colloidal, complexed or adsorbed form. These forms may be included if they can be converted to the dissolved form as evaporation takes place.

(b) The vapor formed is in equilibrium with the liquid at the interface.

(c) The water diffusion is fast enough to ensure that the concentration at the interface is representative of that in the bulk of the water.

(d) The water evaporation rate is not affected by the presence of the PCB.

From these assumptions one can see that the calculations deal with situations in which perfect mixing and equilibration of the liquid phase occur so that as the compound evaporates from the upper layers, no concentration gradients appear. This situation may be approached in reality. However, in many cases, the rate of evaporation will be reduced due to the delay in transference of materials from the mass of water to the depleted interface. Thus, while the calculations

Table 5.10 EVAPORATION PARAMETERS AND RATES FOR VARIOUS AROCLORS AT 25°C

Aroclor	Solubility Mg/liters	Vapor Pressure mm Hg	F^{π}(%)	τ* (for 1 meter depth)
1242	0.24	4.06×10^{-4}	9.7	5.96 hrs.
1248	5.4×10^{-2}	4.94×10^{-4}	46	58.3 min.
1254	1.2×10^{-2}	7.71×10^{-5}	39	1.2 min.
1260	2.7×10^{-3}	4.05×10^{-5}	72	28.8 min.

$^{\pi}$F = the fraction of the mass of PCB present which is evaporated when 0.01% of the water is evaporated.

*τ = the time required for the concentration of PCB to drop to one-half its initial value.

Source: Adapted from Mackay, D., and A. W. Walkoff. 1973. Rate of Evaporation of Low Solubility Contaminants from Water Bodies to Atmosphere. Environmental Science and Technology 7: 611-614.

may be suitable for a fast-flowing, shallow river, they fall short of being representative for a deep, quiescent lake and, in fact, in all cases represent the maximum rates of evaporation achievable. The last column of Table 5.10 presents the calculated half lives (τ) for each respective Aroclor in a column of water 1 m^2 by 1 m deep. The first and second columns tabulate the solubilities and vapor pressures of each mixture that was used to calculate the τ value. In addition, the fraction of PCB present which is lost to the atmosphere when 0.01 percent of the water evaporates is given in the column labeled F.

Thus, in a fast-flowing, shallow river 1 m deep where good mixing occurs, values of τ are quite low, e.g., 5.9 hours for Aroclor 1242 and one-half hour for Aroclor 1260. The authors noted an interesting consequence of this high rate of evaporation. If a monitoring station for municipal or industrial effluents were positioned one hour downstream from a source of Aroclor 1242, by the time the water reached the station, 10 percent of the Aroclor would already have been lost to the atmosphere.

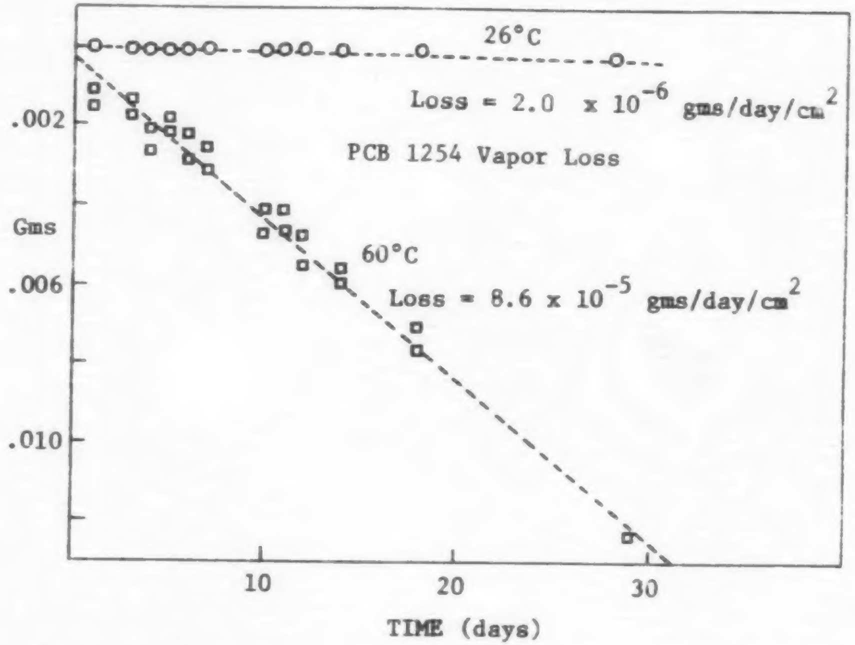
The situation in the Sargasso Sea reflects the importance of evaporation in determining the concentration of PCBs in surface water and atmosphere. The Sargasso Sea is an area of high evaporation and low rainfall and has the lowest surface-water concentrations of PCBs in the North Atlantic (Harvey et al., 1973). It should also be mentioned that the surface layer of the ocean is a major source of atmospheric particulates. Particulates are ejected, both from a central jet and from the ruptured bubble film, when surface bubbles break. Evidence suggests that these particulates are more representative, in composition, of the surface layer than of the bulk of water beneath. Since PCBs concentrate in the surface layer and adsorb to particulates (see Section V.D.3), they are also released to the atmosphere by this mechanism.

2. Air/Soil Interface

The primary source of soil contamination appears to be fallout from the atmosphere (Nisbet and Sarofim, 1972). It has been estimated that 1 to 2 x 10^3 tons per year of the PCBs are released into the atmosphere, adsorb to particulates, and are redeposited on land. By analogy to DDE (a metabolite of DDT), the half life of PCBs in the soil is about five years. All 2 x 10^4 tons of PCB originally deposited into the atmosphere and remaining undegraded were thought to have subsequently been deposited on land. However, through repeated vaporization, readsorption onto particulates, and redeposition, approximately 1/4 of this amount (5 x 10^3 tons) eventually ended up in the ocean. The pattern of deposition of the PCBs will depend to a large extent on the size distribution of the particulates to which they adsorb. The major fraction will end up in coastal waters, but a significant amount will be transported to the open sea.

Some estimate of the rates at which PCBs can be expected to evaporate from various surfaces was provided by Haque et al. (1974). Two types of investigations were carried out. In the first experiment, vapor loss was determined from Aroclor 1254 itself; in the second experiment, the vapor loss was determined following adsorption onto Ottawa and Woodburn soil, two materials exhibiting markedly different adsorbing capacities. The loss of Aroclor 1254 from itself is shown in Figure 5.5. Losses at 26°C are very small, but losses at 60°C are substantial. The loss of PCBs from a sand surface is shown in Figure 5.6. As expected, the percent loss through vaporization decreases as the number of chlorine atoms in the isomers increase. Vapor losses under wet and dry conditions were similar and comparable in magnitude. An identical experiment performed with Woodburn soil revealed that vapor loss from this soil was negligible (no quantitative data presented). The high percentage of organic matter (3.1 percent) in this soil contributes to its adsorbing capacity and is probably responsible for the observed result.

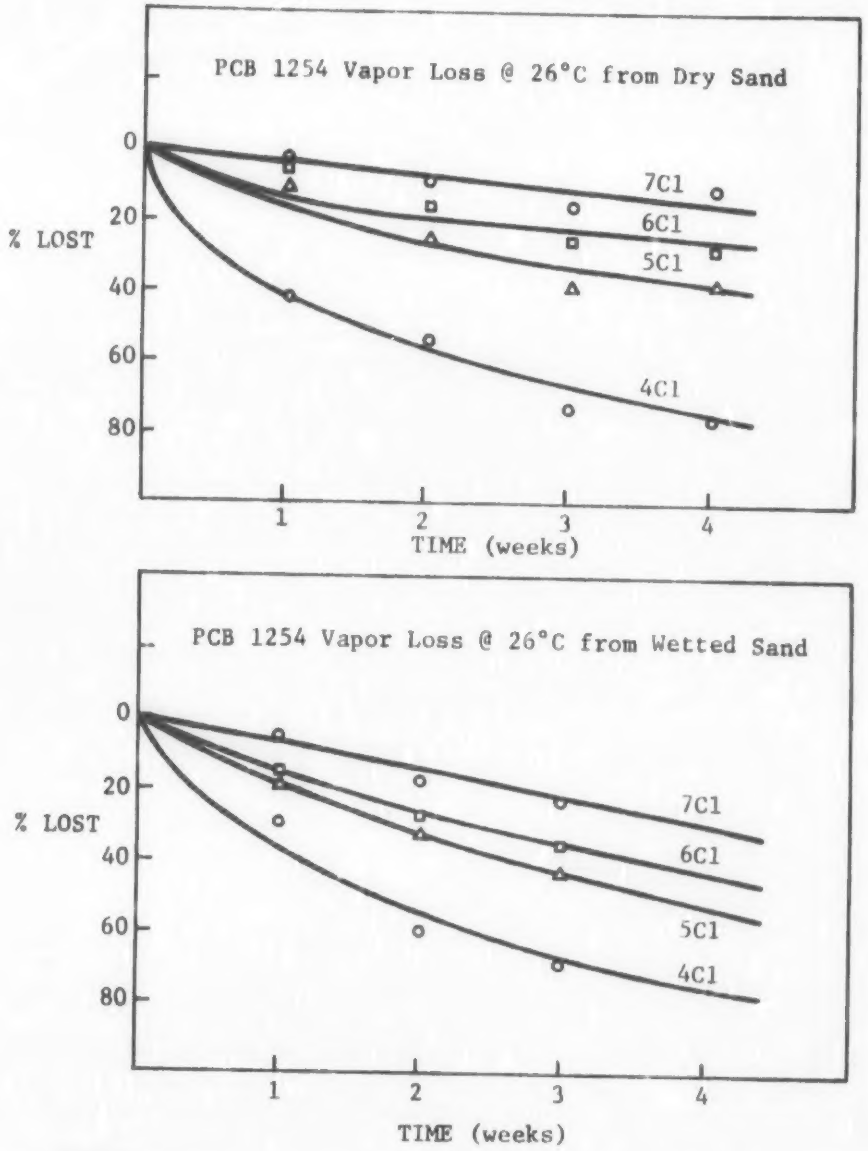
From these experiments, some conclusions may be drawn about transport at the soil/air interface. Adsorption to a surface will be influenced by such factors as surface area, organic content of the material, and nature of the material (e.g., soil, sand, etc.). The transport of PCBs in the atmosphere will, in turn, be influenced by such factors as temperature and vapor pressure. Significant amounts of PCB could be lost to the air at higher temperatures if PCBs are present in the lithosphere free, loosely bound, or adsorbed to a surface. A PCB mixture containing a large percent of the lower-chlorinated isomers will experience greater loss into the atmosphere



Source: Haque, R., D. W. Schmedding, and V. H. Freed. 1974. Aqueous Solubility, Adsorption and Vapor Behavior of Polychlorinated Biphenyl Aroclor 1254. Environmental Science and Technology 8: 139-142.

FIGURE 5.5

LOSS OF AROCLOR 1254 FROM ITSELF AS A FUNCTION OF TIME



Source: Haque, R., D. W. Schmedding, and V. H. Freed. 1974. Aqueous Solubility, Adsorption and Vapor Behavior of Polychlorinated Biphenyl Aroclor 1254. Environmental Science and Technology 8: 139-142.

FIGURE 5.6

LOSS OF AROCLOR 1254 FROM AN OTTAWA SAND than one containing the more highly chlorinated isomers. Strongly bound PCBs, on the other hand, will be lost only to a slight extent.

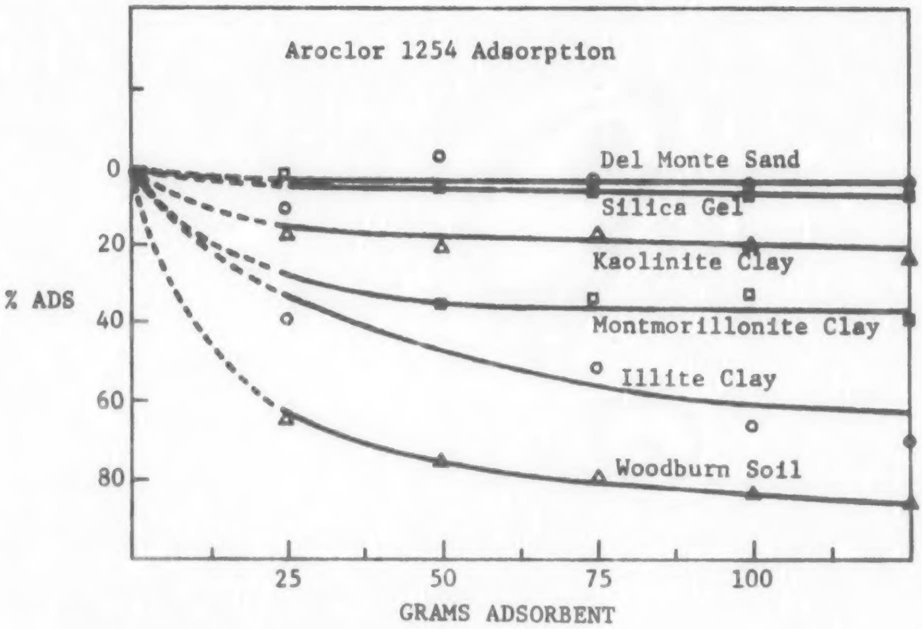
3. Soil/Water Interface (including sediment)

Because of their low solubility, high specific gravity, and tendency to adsorb to particulates, the majority of PCBs released into the hydrosphere are expected to eventually end up adsorbed onto sediment or resting as sludges at the bottom of rivers and lakes and in the oceanic abyss (Nisbet and Sarofim, 1972). Nisbet and Sarofim estimated that all of the 2 x 10^4 tons of PCBs discharged into fresh water between 1930 and 1970 could be found in the sediment. Transport in rivers is thought to take place by solution and readsorption onto sediment and by the transport of sediment itself. Approximately 200 tons/year of PCBs are transported to the ocean by this pathway and the sediment of the deep oceans represents the ultimate sink for PCB residues.

Several laboratory studies have been reported that demonstrate the tenacity of PCBs for a variety of surfaces and particulates. Eichelberger (1971) added 10 μg of each Aroclor (from 1232 to 1268) individually to 1 liter of river water in glass containers, sealed each container with a teflon-coated cap, and sampled the water for PCB concentration periodically for 16 weeks. Approximately 40 percent of the PCBs remained in solution at this time. Evaporation was eliminated as the pathway of loss because the bottles were tightly sealed. Also, since the Aroclors were recovered intact, biodegradation could also be eliminated. It was concluded that irreversible adsorption onto the walls of the sample container and/or the silt present in the river water was responsible for the disappearance.

An interesting study performed by Haque et al. (1974) investigated the behavior of a saturated aqueous solution of Aroclor 1254 (56 ppb) in the presence of increasing amounts of adsorbed materials. The results are presented in Figure 5.7. Illite clay and Woodburn soil showed the greatest adsorbance; montmorillonite and kaolinite clays were intermediate; and sand and silica gel adsorbed very little of the dissolved PCBs, even at high concentrations. The high adsorbing capacity of the Woodburn soil was attributed to the presence of organic matter. Thus, the concentration of PCBs in water will be reduced whenever the water comes in contact with particulate matter. The extent of reduction will depend on the adsorption characteristics of the particulate matter involved. A sand surface with few adsorbing sites adsorbs relatively little, whereas a soil surface with high clay and organic content will adsorb significant amounts.

These experiments are relevant not only to the partitioning of PCBs between water and sediment but also to that between precipitation, irrigation waters, or leachate and soils. If PCBs should come into contact with the terrestrial environment by any of these routes, the nature of the surface will determine whether the PCB will be adsorbed and, therefore, contained or will be allowed to progress to other areas. The study by Tucker et al. (1975a), in which the extent to



Source: Haque, R., D. W. Schmedding, and V. H. Freed. 1974. Aqueous Solubility, Adsorption and Vapor Behavior of Polychlorinated Biphenyl Aroclor 1254. Environmental Science and Technology 8: 139-142.

FIGURE 5.7

PERCENT DECREASE IN THE CONCENTRATION OF AROCLOR 1254 BY THE ADDITION OF INCREASING AMOUNTS OF ADSORBENT TO A SATURATED (56 ppb) SOLUTION which PCBs were removed from various types of soil by percolating water (see Section IV.C) was investigated, in general confirmed the above conclusions. Soils with a high clay content retained the PCBs most effectively. Contamination of ground water supplies are, therefore, most likely when the PCBs travel through permeable sand and creviced bedrock formations where they may progress at rates of several thousand feet per year (Walker, 1973).

A study of the behavior of PCBs (as Aroclor 1260) in natural waters from two sources when their respective sediments were also present was reported by Oloffs et al. (1973). The sources of the water and sediments were the Fraser River and the Georgia Strait, British Columbia. Bottom sediment (100 g) from each source was placed in a 500 milliliter (ml) Erlenmeyer flask. One hundred and fifty ml of water from the same source containing 0.1 ppm PCB (Aroclor 1260) was carefully layered over the sediment. The flasks were plugged with glass wool and allowed to stand for 12 weeks. Water and sediment were analyzed for PCB at 0, 6, and 12 weeks. The results are presented in Table 5.11. All detectable residues had moved out of the water by six weeks and an average of 73.8 percent and 73.2 percent could be detected in the sediment from the Fraser River and Georgia Strait, respectively. No residues could be extracted from the glass wool plug, suggesting that evaporation was negligible. The 25 percent of the PCBs that was unaccounted for most likely was adsorbed to the glass walls of the Erlenmeyer flask. This study should be compared to that

Table 5.11 FATE OF 0.1 ppm AROCLOR 1260 IN 150 ml WATER SAMPLES FROM FRASER RIVER AND FROM GEORGIA STRAIT IN THE PRESENCE OF BOTTOM SEDIMENTS FROM THE SAME SOURCES, INCUBATED AT 13°C

Recovery in %

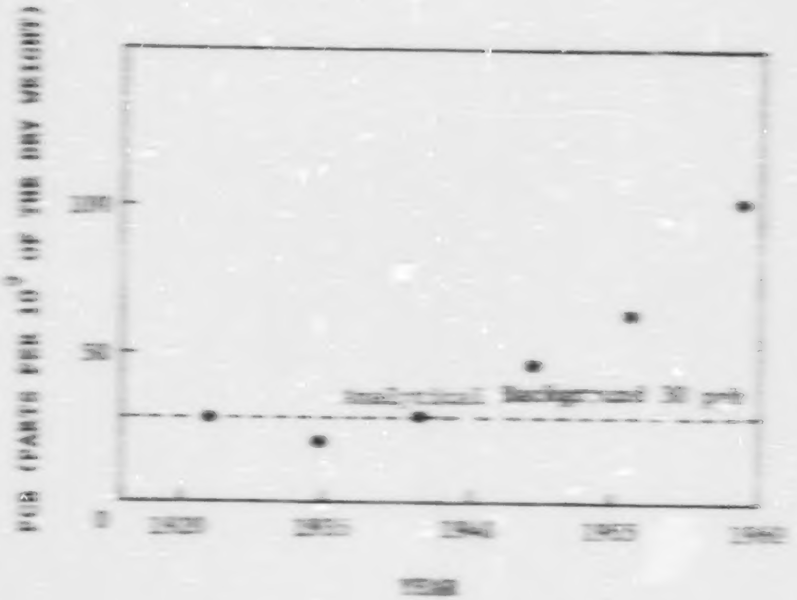
Incubation time (weeks)	Fraser River		Georgia Strait	
	Water	Sediment	Water	Sediment
0	100	0	100	0
6	0	70.4	0	70.6
6	0	67.1	0	71.1
12	0	72.8	0	80.7
12	0	74.7	0	65.6

(No residues could be detected on the silanized glass wool plugs used to stopper flasks during incubation. Controls (0-12 weeks) were free from detectable residues.)

Source: Adapted from Oloffs, P. C., L. J. Albright, S. Y. Szeto, and J. Lau. 1973. Factors Affecting the Behavior of Five Chlorinated Hydrocarbons in Two Natural Waters and Their Sediments. Journal of Fisheries Research Board of Canada 30: 1619-1623.

of Oloffs et al. (1972) in which it was shown that Aroclor 1260 escaped from the same natural waters into the atmosphere when incubated under identical conditions in the absence of bottom sediment (see Section V.D.1). Apparently, when PCBs are present in natural waters not in contact with their bottom sediments, loss into the atmosphere at the water-air interface is significant. However, if the water is in contact with bottom sediment, adsorption onto the sediment occurs preferentially. The depth of water probably influences the net outcome of these two opposing processes.

The implications of these laboratory studies are borne out in the environment. Hom et al. (1974) analyzed dated oceanic sediment from the Santa Barbara Basin of the Southern California Bight for PCB residues. The layered anaerobic sediments of this area provide a situation in which the rate of deposition of PCBs throughout the years can be determined. The results are presented in Table 5.12 and shown graphically in Figure 5.8. The gas chromatographic profiles of all samples resembled Aroclor 1254 which, consequently, was used as a reference standard. Analytical background levels were approximately 30 ppb (limit of detection). It can be seen that deposition of PCBs began about 1945 and increased consistently through 1967 with no indication of a leveling off taking place. Since about 0.39 cm of sediment are laid down per year with a mass of 0.1 g per cubic cm (determined by Hom et al., 1974), it can be calculated that the 1967 PCB concentration of 103 ppb is equivalent to a deposition rate of:



Source: Hom, W., R. W. Risebrough, A. Soutar, and D. R. Young. 1974. Deposition of DDE and Polychlorinated Biphenyls in Dated Sediments of the Santa Barbara Basin. *Science* 184: 1197-1199.

FIGURE 5.3

DEPOSITION OF PCB IN DATED SEDIMENTS OF THE SANTA BARBARA BASIN

Preceding page blank

$$103 \times 10^{-9}\ (\text{ppb}) \times 0.3\ \text{g/cm}^3 \text{ of deposit} \times 0.39\ \text{cm/year} \times 10^4\,\text{cm}^2/\text{m}^2 =$$
$$1.2 \times 10^{-4}\ \text{g/m}^2/\text{year} = 120\ \mu\text{g/m}^2/\text{yr}.$$

This figure is assumed to represent a minimum estimate of the rate of loss of these compounds into the overlying waters. Deposition into sediment is thus a major pathway for the removal of PCBs from marine waters.

Duke *et al.* (1970) analyzed the water and sediment of Escambia Bay, Florida, during and after leakage of Aroclor 1254 from an air compressor which contaminated the water. The highest concentrations of PCBs in the water occurred at the outfall in the Escambia River in August 1969 (275 ppb) and decreased dramatically to 3 ppb in September when the leakage was corrected. Slightly less than 3 ppb could still be found in October 1969. The continued presence of PCBs in the water months after the leakage was stopped was attributed to leaching from the sediment. PCB residues reached 486 ppm in August 1969 (1767 times that in water) in sediment samples taken close to the outfall but have decreased since then (no value given).

Samples of water and bottom sediment were collected from six sites on Lake Poinsett and Dry Lake, South Dakota, and analyzed for PCBs (Greichus *et al.*, 1973). The average value in the water from six samples was <0.5 ppb, whereas that of the sediment was 6.4 ppb, representing concentration in sediment by a factor of about 13.

Law and Goerlitz (1974) reported the results of a study initiated by the U.S. Department of the Interior in which contamination by chlorinated hydrocarbons (including PCBs) was investigated in the numerous streams that discharge into the San Francisco Bay. Bottom sediment from 26 streams (39 sites, total) was collected and analyzed for PCBs. The results are presented in Table 5.13. PCB residues were found in all of the streams tested and are, therefore, widely dispersed throughout the San Francisco Bay area. Values ranged from less than 1 µg/kg to 1400 µg/kg. Stevens Creek (180 µg/kg) and Alamitos Creek (610 µg/kg) had values much greater than expected since neither stream is located near an industrial or commercial development.

Data gathered by the Geological Survey, U.S. Department of the Interior, in the course of pesticide residue monitoring is seen to reflect the widespread occurrence of PCB residues in bottom sediments throughout the country (Crump-Wiesner *et al.*, 1974). Samples were taken from lakes and streams generally located away from industrial centers. The results are presented in Table 5.14. Of samples collected at random from 16 states, 11 states had positive samples containing PCB residues at levels ranging from 5 to 2400 µg/kg. One out of every five bottom sediments across the nation contained PCBs. Data from Florida (not shown on the table) revealed that 12 out of 231 water samples (5 percent) contained PCB residues at levels of from 0.1 to 2.1 µg/kg (median concentration, 0.2 µg/kg). Of 118 samples of bottom sediment analyzed, 50 (42 percent) contained PCBs at levels of from 5 to 3200 µg/kg (median concentration, 30 µg/kg). Once again,

Table 5.15 PCB RESIDUES FOUND IN SAN FRANCISCO BAY AREA STREAMS

SITE NO.	STREAM	PCB RESIDUE CONCENTRATION IN µG/KG[1,2]
1	Colma Creek	1.9
2	Colma Creek	12
3	Belmont Creek	52
4	Cordilleras Creek	16
5	Cordilleras Creek	6.0
6	Redwood Creek	21
7	San Francisquito Creek	1.2
8	San Francisquito Creek	130
9	Los Trancos Creek	21
10	Stevens Creek	180
11	Stevens Creek	30
12	Los Gatos Creek	5.0
13	Los Gatos Creek	120
14	Guadalupe River	137
15	Guadalupe River	2.7
16	Alamitos Creek	710
17	Coyote Creek	15
18	Coyote Creek	12
19	Alameda Creek	11
20	Alameda Creek	30
21	Arroyo de la Laguna	160
22	Arroyo de la Laguna	33
23	San Lorenzo Creek	25
24	Wildcat Creek	21
25	Wildcat Creek	53
26	San Pablo Creek	37
27	Pinole Creek	150
28	Green Valley Creek	[3]
29	Napa River	8.8
30	Napa River	1400
31	Napa River	7.6
32	Sonoma Creek	5.0
33	Petaluma River	27
34	Novato Creek	10
35	Miller Creek	31
36	San Rafael Creek	150
37	Corte Madera Creek	81
38	Corte Madera Creek	11
39	Arroyo Corte Madera del Presidio	25

[1] Based on oven-dry weight of stream bed material uncorrected for percent recovery.

[2] Underlined values indicate mass spectrometric confirmation of residue identity.

[3] The presence of 55 µg/kg of polychlorinated naphthalenes (PCN) obscured any PCBs present. PCN was identified by gas chromatograph/mass spectrometer.

Source: Adapted from Law, L.M. and Goerlitz, D.F., 1974
Selected Chlorinated Hydrocarbons in Bottom Material from Streams Tributary to San Francisco Bay. *Pesticides Monitoring Journal* 8:33-36.

Table 5.14 SUMMARY OF PCB RESIDUE DATA FOR BOTTOM SEDIMENTS, JANUARY 1971–JUNE 1972

State	No. Samples	Occurrences	Concentration, µg/kg	Median Concentration, µg/kg
Alaska	5	0	ND	ND
Arkansas	5	4	20–2,400	60
California	13	3	20–190	85
Connecticut	1	1	40	ND
Hawaii	4	0	ND	ND
Georgia	12	10	10–1,300	300
Maryland	11	5	10–1,200	30
Mississippi	8	2	50;170	ND
New Jersey	12	10	8–250	20
Oregon	4	2	15;140	ND
Pennsylvania	16	11	10–50	20
South Carolina	11	8	30–200	50
Texas	293	21	7.9–290	80
Virginia	15	8	5–80	40
Washington	10	0	ND	ND
West Virginia	2	1	10	ND

NOTE: ND = not detected.

Source: Crump-Wiesner, H. J., H. R. Feltz, and M. L. Yates. 1974. Pesticides in Water: A Study of the Distribution of Polychlorinated Biphenyls in the Aquatic Environment. *Pesticide Monitoring Journal* 8: 157-161.

It can be seen that PCBs accumulate in sediment to anywhere from 2.6 to 32,000 times their concentration in water.

The affinity of PCBs for sediment has been invoked to explain the absence of an in-shore to open-ocean concentration gradient in the surface waters of the North Atlantic (Harvey *et al.*, 1973; Harvey *et al.*, 1974) when such a gradient exists in the atmosphere (Harvey and Steinhauer, 1974). Since more PCBs are being delivered to the coastal regions than to the open ocean, via the atmosphere, higher concentration would be expected in coastal waters. However, the higher particulate concentration in the coastal waters (100 times greater than that in the open ocean) along with a more rapid sedimentation rate enables a larger proportion of those PCBs delivered to coastal areas to be adsorbed and sedimented out of the water. Therefore, while most of the PCBs delivered to the open ocean remain in solution, a good percentage of those delivered to the coastal regions are deposited in the sediment. The net result is the absence of any discernable concentration gradient.

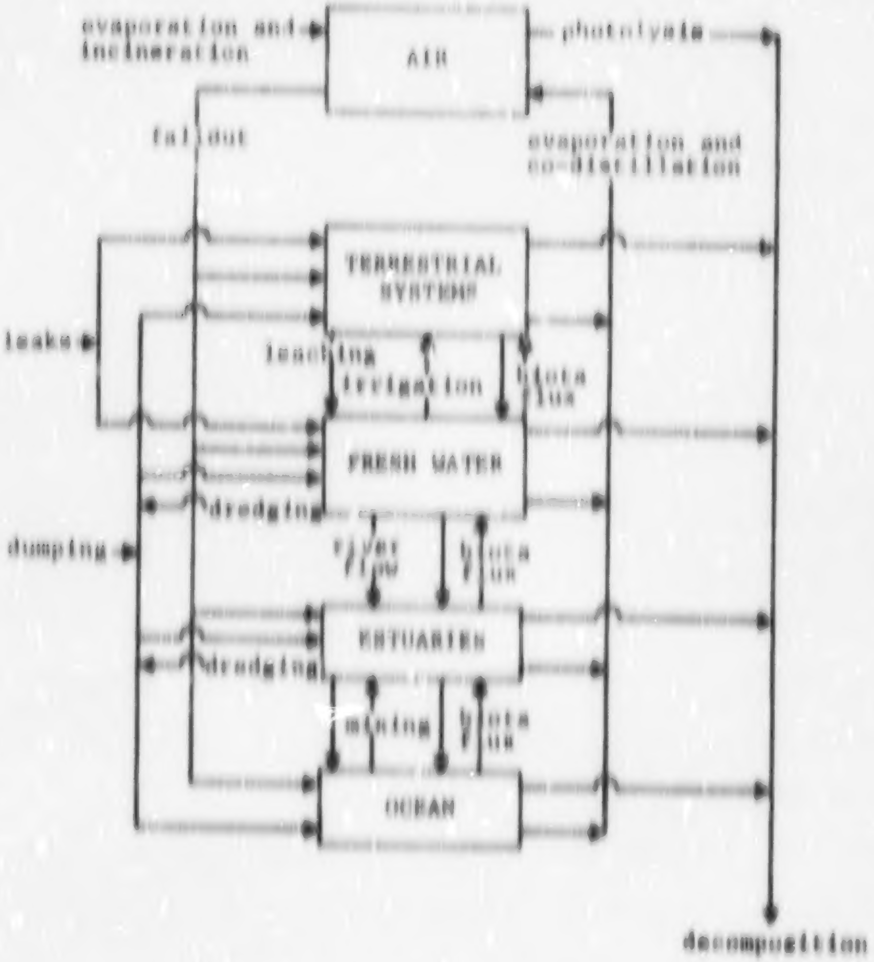
B. TRANSPORT MODELS

The function of a transport model for a chemical pollutant is to provide us with information as to the fate of that pollutant in the environment. The model must trace the substance in question from its entry into each susceptible environmental compartment, through its transfer (if any) between compartments, to its decomposition (if any) within compartments, and finally to its ultimate sink(s).

An accurate model will successfully account for present levels of the pollutant in each compartment and will correctly predict the alterations in environmental concentrations resulting from a change in input.

Assuming that PCBs are similar in behavior to DDT, Nisbet and Sarofim (1972) proposed a transport model which has held up reasonably well in the face of evidence, both experimental and analytical. All of the evidence and most of the results have been presented in the previous sections of this chapter and will only be briefly reviewed at this time. The reader should refer to the appropriate section for details as to quantities of material released and transported by each mechanism and the relative importance of each pathway as a source of contamination. The model proposed by Nisbet and Sarofim is presented in Figure 5.9. This model was based on pathways into the environment prior to 1971, some of which are presumably no longer a source of concern. However, the significant concentrations of PCBs found in the atmosphere and hydrosphere (see Sections V.B. and V.C) years after the supposed discontinuation of their use for dispersive applications suggest that these pathways may still be operative. Gross estimates of the rates of input via each pathway based on the interpretation of 1970 sales figures and assumptions as to the useful life span of PCB-containing products are summarized in Table 5.11.

PCBs are released directly to the atmosphere via vaporization from products, evaporation from themselves, or incomplete


evaporation and incineration
AIR
photolysis
fallout
evaporation and co-distillation
TERRESTRIAL SYSTEMS
leaks
leaching
irrigation
biota flux
FRESH WATER
dredging
dumping
river flow
biota flux
ESTUARIES
dredging
mixing
biota flux
OCEAN
decomposition

Source: Nisbet, I. C. T., and A. F. Sarofim. 1972.
Rates and Routes of Transport of PCBs in The Environment.
Environmental Health Perspectives Exp. 1: 21-38.

FIGURE 5.9

ENVIRONMENTAL TRANSPORT MODEL

TABLE 5.15 GROSS ESTIMATES OF RATES IN INPUT AND ACCUMULATION OF PCBS IN NORTH AMERICA IN 1971

Category of Input	Rates (tons/year)	PCB Grade	Compartment Affected
Vaporization of plasticizers	$1-2 \times 10^3$	Mainly 1248 to 1260	atmosphere
Vaporization during open-burning	4×10^2	Mainly 1242	atmosphere
Leaks and disposal of industrial fluids	$4-5 \times 10^3$	1242 to 1260	hydrosphere
Disposal in dumps and landfills	1.8×10^4	1242-1260	lithosphere
Accumulation in services	7×10^3	1242-1254	-

Source: Adapted from Nisbet, C. T. and A. F. Sarofim. 1972. Rates and Routes of Transport of PCBs in the Environment. *Environmental Health Perspectives* Exp. 1: 21-38.

incineration. Nisbet and Sarofim estimated that 1500 to 2500 tons per year are released into the environment by this pathway. The PCBs are carried through the air predominantly in the vapor phase (Bidleman and Olney, 1974a) or adsorbed onto particulates and may travel great distances in this form. It is thought that the atmosphere provides the major route of transport for PCBs throughout the environment (Södergren, 1972; Oloff et al., 1972; Mackay and Wolkoff, 1973; Harvey and Steinhauer, 1974). PCBs are then deposited on land or into fresh and marine waters by particle sedimentation or rainout (estimated total fallout, 1000 to 2000 tons/year). The greatest loss to the atmosphere occurs in industrialized or urban areas, and decreasing concentration gradients in air are observed from the coast out to the open ocean (Harvey and Steinhauer, 1974). Fallout onto land and water is also greatest in these areas, close to the sources of emission. Re-evaporation from the lithosphere and hydrosphere is a further source of atmospheric contamination. The extent of vaporization from terrestrial surfaces will depend upon many factors, including the nature of the surface. Losses will be greatest from surfaces such as sand and small from soils with a high organic matter content (Haque et al., 1974). Evaporation and codistillation from the surface layer of bodies of water where PCBs accumulate due to the high lipid content of the surface microlayer may be significant. Shallow, fast-flowing rivers and streams where depleted surface layers are constantly renourished will experience the greatest loss of PCBs by this route (Mackay and Wolkoff, 1973).

Dumping of wastes in the liquid form via industrial and municipal waste water effluents (4 to 5 x 10^3 tons/year) or in the solid form as sewage sludge, solid waste, and dredge spoil (maximum 400 tons/year) are further sources of contamination to both lithosphere and hydrosphere. Accidental spills and leaks should also be included in this category. Although leaching from sanitary landfills and garbage dumps (which accumulate 1.8 x 10^4 tons of PCBs annually) is theoretically possible, evidence suggests that losses by this route are, in fact, negligible. Leaching from certain terrestrial surfaces such as sand and creviced bedrock into groundwater supplies is, however, a more likely source of contamination as is leaching from paints and surface coatings in contact with moist food products, e.g., silos painted with coatings containing PCB. The reverse type of contamination, that is, contamination of terrestrial compartments via irrigation, is a distinct possibility, especially if the water is taken from a highly industrialised area. Contamination by this pathway was estimated to amount to about 15 tons per year.

The fate of PCBs delivered to both fresh and marine waters is adsorption onto particulate matter and, ultimately, deposition into bottom sediment. Transport of PCBs in rivers to estuaries and the open sea takes place by solution and readsorption onto particulates and by the transport of sediment itself and was estimated to amount to about 200 tons per year. PCBs dissolved in relatively shallow water, in which there is close contact with bottom sediment, will adsorb onto the sediment rather than move to the surface layer and evaporate into the atmosphere. Only in deep waters does evaporation compete successfully with particulate scavenging and sedimentation (Oloffs et al., 1973).

PCBs may also travel through the environment via biota flux and food chains. PCBs entering food chains may eventually end up in migratory species which may transport them to relatively uncontaminated areas.

In any transport model, pathways of decomposition and other avenues of disappearance from the biosphere must be considered. Since, in general, the water solubilities and vapor pressures of the various PCB isomers decrease with increasing chlorine content, the lower isomers will more readily be dissolved, evaporated, and codistilled. The net result is a fractionation of PCB isomers with the higher isomers exhibiting less mobility than the lower ones. This fact may contribute to the observation that gas chromatographic profiles of PCBs from contaminated environmental samples are frequently rich in the higher isomers and usually resemble Aroclor 1254 or 1260 (Veith and Lee, 1971). The lower isomers also undergo metabolic degradation by microorganisms, probably the major cause of their removal from the biosphere. Photolytic decomposition of some PCB isomers in natural sunlight has been reported (Risebrough et al., 1968; Safe and Hutzinger, 1971; Hutzinger and Safe, 1972b; see Section II.C). Apparently some higher isomers are broken down more easily than the lower isomers; perhaps contributing to the observed relative abundance of lower isomers in atmospheric samples (Bidleman and Olney, 1974a). In addition, photolytic dechlorination is also expected to give rise to lower isomers (Hutzinger and Safe, 1972). Due to the high stability of PCBs, other non-biological forms of decomposition are expected to be extremely slow or negligible.

Nisbet and Sarofim concluded that most PCB isomers with four or fewer chlorine atoms released into the environment have been degraded, primarily by microbial decomposition; consequently, about 75 percent of the Aroclor 1242 released, 60 percent of Aroclor 1248, 20 percent of Aroclor 1254, and 5 percent of Aroclor 1260 have disappeared.

Assuming that the proportion of PCB sales for different applications remained constant between 1930 and 1970 and that the percentage lost during this period was identical to that reflected in Table 5.15 for the year 1970, Nisbet and Sarofim estimated that cumulative losses to the environment were 3 x 10^4 tons to the atmosphere, 6 x 10^4 tons into fresh and coastal waters, and 3 x 10^5 tons into dumps and landfills. From the grade of PCB released into each compartment (Table 5.15) and the estimated percentage decomposition of each grade, it can be concluded that roughly one-third of the PCBs released into the atmosphere and one-half of those released into the hydrosphere during the period in question have now been degraded. Little can be said about those PCBs disposed of in landfills since they were often in sealed containers and, therefore, not available for bacterial degradation.

Thus, 2 x 10^4 tons of the PCBs released into the atmosphere and 3 x 10^4 tons of the PCBs released into the hydrosphere between 1930 and 1970 remain in the environment. Of the remaining PCBs originally released into the atmosphere, about one-quarter (5 x 10^3 tons) are expected to have been transferred to the sea; the rest (1.5 x 10^4 tons) were deposited in the lithosphere. Of the remaining PCBs originally released into the hydrosphere, 2 x 10^4 tons are expected to have accumulated in the sediment of rivers and lakes (a small amount, 10^2 tons, is in solution in fresh waters) and 10^4 tons to have reached the sea. These results are summarized in Table 5.16.

It is believed that, due to precautions presumably being taken by manufacturers and consumers and to the voluntary restriction of sales for dispersive applications, the major input of PCBs into the environment has already occurred. However, present atmospheric and hydrospheric samples suggest that a significant amount is still entering the biosphere. PCBs are widespread and chemically stable. Thus, even if a total cessation of both their manufacture and use were possible, it would be many years before the environment would rid itself of these compounds.

Table 5.16 PCB ACCUMULATION BETWEEN 1930 AND 1970

Reservoir	PCB Accumulation (tons)
Soil (excluding dumps)	1.5×10^4
Oceans (adjacent to North America)	1.5×10^4
Fresh water (dissolved or in suspension)	10^2
Fresh water sediment	2×10^4
Dumps and landfills	3×10^5

Source: Adapted from Nisbet, C. T. and A. F. Sarofim. 1972. Rates and Routes of Transport of PCBs in the Environment. Environmental Health Perspectives Exp. 1: 21-38.

VI. CONTROL OF PCBs IN THE ATMOSPHERE

A. SUMMARY

Proper safeguards will minimize the loss of PCBs to the environment. All PCBs should be handled, shipped, and used in closed systems. However, some escape of PCBs from such systems is inevitable as the result of spills, leaks, accidents, and equipment malfunction.

Workers are protected by good housekeeping procedures in the plant; these will minimize PCB loss to the working environment and ensure containment and prompt cleanup of spills. Protective clothing and adequate ventilation systems are specific controls that safeguard the worker.

Loss of PCBs to the environment can occur during manufacture, in consumer industries during use, and during disposal. PCBs may enter directly through the atmosphere, lithosphere, or hydrosphere but, because of media distribution and transport patterns, these realms are interconnected and PCBs are present in all three.

PCB losses to the atmosphere can be controlled rather effectively if the PCBs are handled, used, and disposed of properly. PCB losses to the lithosphere can theoretically be controlled, although accidents will always be a prime source; a major problem is the installation of controls for transformers and capacitors that are already installed. Control of PCB losses to the hydrosphere is currently the least effective. Although there are some promising developments, apparently there is now no technology that can ensure zero PCB discharge from a point-source effluent. Control is, therefore, best effected by preventing contamination of sewage.

The controls that are currently available should be evaluated for effectiveness, cost benefit, etc. New controls and technology should be developed and evaluated and then made available as soon as possible. There is a need for a manual that will detail the hazards of PCBs and the recommended procedures for the handling, use, and disposal of PCBs and PCB-contaminated materials. This manual should list controls, methods, devices, materials, and technologies that are available for controlling the loss of PCBs to the environment. This manual should be distributed widely and should be readily available.

B. INTRODUCTION

Workers may be exposed to PCBs at production facilities, in consumer industries, and wherever PCB-containing products are used. If the American National Standards Institute (ANSI) guidelines (1974) are followed, worker exposure should be nil inasmuch as the recommended procedures entail use of closed systems for the manufacture, transport, and handling of PCB-containing askarels (non-flammable dielectric insulating fluids). Nevertheless, even when these guidelines are followed, workers may still be exposed to PCBs as a consequence of equipment malfunction or breakdown, leaks, spills, and various accidents.

The general populace is exposed to PCBs when PCBs enter the ambient environment from the working environment or from use of products containing PCBs. This can occur when the recommended procedures are not followed, when leaks and spills are not contained and cleaned up, and when PCBs and PCB-contaminated items are not disposed of properly. Any of these events introduce PCBs into the atmosphere and/or lithosphere and/or hydrosphere.

C. CONTROL OF PCB LOSSES AT PRODUCTION FACILITIES AND BY CONSUMER INDUSTRIES

1. Methods for Control of Worker Exposure

The American Conference of Governmental Industrial Hygienists (1964, 1973) has recommended that the maximum atmospheric concentration per eight-hour workday be 1.0 mg chlorodiphenyl (42 wt % Cl) per cubic meter of air and 0.5 mg chlorodiphenyl (54 wt % Cl) per cubic meter of air. Air monitoring is probably not necessary inasmuch as the odor of PCBs is strong, very unpleasant, and irritating at concentrations that are much lower than the threshold value, and consequently the odor threshold would provide ample warning of the presence of PCB vapor (Papageorge, 1975). Nevertheless, Monsanto does monitor for PCBs (levels are non-detectable in the working environment), and it is also developing a portable, battery-operated detection unit to be carried by each individual worker (Papageorge, 1975).

The American Industrial Hygiene Association (AIHA) (1965) recommends the use of chemical cartridge respirators or gas masks approved by the U.S. Bureau of Mines should worker exposure to higher concentrations of PCBs be unavoidable (e.g., in the event of leaks or spills of hot fluids). The ANSI guidelines (1974) cite the need for maintenance of gas masks, respirators, and replacement parts on a regular basis. Monsanto (1975b) specifies that when hot askarel must be handled in a closed or confined area, the area should be provided with mechanical exhaust ventilation or the workers should wear an organic cartridge respirator approved by the U.S. Bureau of Mines. The instructions of the U.S. Army Environmental Hygiene Agency (1975) specify adequate ventilation of 150 cubic feet per minute per square foot of area when hot askarels (≥55°C) are handled.

Prolonged or repeated skin exposure to PCBs should be avoided (AIHA, 1965). The Institute of Electrical and Electronics Engineers (IEEE, 1974) recommends that no type of glove be used. On the other hand, ANSI (1974) specifies that porous gloves be avoided and that barrier creams or resistant gloves be used. Similarly, the use of chemical gloves is recommended in the General Motors guidelines (1974) and by the U.S. Army Environmental Hygiene Agency (1975). Exposed skin surfaces should be washed thoroughly and immediately with soap and water (AIHA, 1965), and then cold cream (ANSI, 1974; IEEE, 1974) or silicone-bearing hand lotion (IEEE, 1974) should be applied.

When the splashing of askarels is possible, workers should use eye protection such as glasses or shields (IEEE, 1974) or safety glasses with side shields or face shields (ANSI, 1974; General Motors, 1974). If askarel does contact the eye, then the recommended first aid is flushing the eye with large quantities of water (Monsanto, 1975b) for 15 minutes (AIHA, 1965; ANSI, 1974) followed by application of castor oil (ANSI, 1974; IEEE, 1974; Monsanto, 1975b). The worker should see a physician who may prescribe an ophthalmic anesthetic solution to relieve irritation and inflammation (AIHA, 1965; Monsanto, 1975b).

In General Motors plants, workers use chemical aprons to protect their clothing from askarel (General Motors, 1974). Monsanto provides its workers with work clothing (Papageorge, 1975). Contaminated clothing should be removed promptly (AIHA, 1965), and subsequently it should be dry-cleaned (Monsanto, 1975b) or otherwise properly laundered or disposed of (ANSI, 1974). The U.S. Army Environmental Hygiene Agency (1975) instructions specify that lightly contaminated clothing can be laundered in warm soapy water with the wastewater "discharged to the sanitary sewer at a rate consistent with the 1972 Environmental Protection Agency proposals to keep PCB levels in rivers and lakes below 0.01 ppb," whereas saturated clothing should be stored in steel drums prior to disposal by incineration.

Ingestion of askarels is not a problem in industry (ANSI, 1974). Good personal hygiene habits will greatly reduce this possibility. The ANSI guidelines (1974) state specifically that workers should wash their hands with soap and warm water before eating, drinking, smoking, and using toilet facilities.

The AIHA (1965) recommends that persons who are regularly or repeatedly exposed to PCBs should be examined periodically for evidence of skin irritation and/or liver damage. ANSI (1974) was less stringent; its guideline specifies that a person who develops a skin irritation or respiratory tract irritation while working with askarel should be placed under the supervision of a physician.

It should be noted that this section is limited specifically to those aspects of control of worker exposure to PCBs that pertain to the worker's person, clothing, and immediate working environment as well as personal health and hygiene. Obviously, the conditions in the plant and the general working environment (which are discussed below in Sections VI.C.2, VI.D.1, and VI.D.2) have a direct bearing on the worker.

2. Methods for Control of External Emissions

The recommendations of both ANSI (1974) and Monsanto (1975b) emphasize that proper handling of askarels containing PCBs necessitates the use of closed and sealed systems that will prevent the entry of PCBs into the environment. ANSI (1974) and Monsanto (1975b) as well as the IEEE (1974) have published specifications for piping, hoses, connections, gaskets, valves, packing, cements, storage and shipping drums, and tank cars that are used in the handling/transport of PCBs.

In addition, certain basic precautions should be taken (ANSI, 1974; Monsanto, 1975b) which involve general good housekeeping procedures based on the necessity for keeping all PCBs as well as all PCB-contaminated items separate and apart from non-contaminated materials. This entails separation, containment, and proper disposal of all PCB-contaminated material.

Even if all these guidelines are followed closely, control methodology must be available because leaks, spills, and other accidents do occur. Prompt and proper cleanup procedures will effectively keep PCBs from the environment.

Although the primary subject of this study is PCBs in the atmosphere, the transport and transformation of PCBs in other media oblige us to consider as well control methodology for the lithosphere and for the hydrosphere.

a. Losses to Atmosphere. Monsanto (1973b) has endeavored to eliminate the emissions of PCBs to the atmosphere from the manufacturing area. Rupture disc lines and atmospheric vents were rerouted through catch tanks or to settling basins. Mist eliminators (Brink Mist Eliminator, Enviro-Chem Systems Company) were placed in all vapor lines; these serve to condense and collect the PCB vapors (Papageorge, 1975). Use of the Brink Mist Eliminator in the ventilating system prevents escape of PCBs into the air from the manufacturing area to other parts of the plant and to the atmosphere. Storage tanks are blanketed in nitrogen to eliminate "breathing" (Monsanto, 1973b). In addition, all air from the ventilating system is passed through the incinerator (Papageorge, 1975).

General Electric has eliminated pouring and the use of open containers of PCBs in the process of filling transformers. Thus, all PCBs are now handled in a closed system, and the askarel is drawn by vacuum into the previously evacuated transformer (Bachli, 1975).

Monsanto (1975b) specifies that all tank cars must be unloaded through the top (dome fitting) by pumping or with controlled pressure using dry air or dry nitrogen. This technique prevents loss of PCBs to the atmosphere during the loading and unloading of tank cars. Loading and shipping safeguards are included in specific written instructions on every container (Monsanto, 1973b).

An activated carbon unit (e.g., VentSorb by Calgon Corporation) hooked up to the vent of a storage tank would effectively prevent the release of PCBs to the atmosphere from such a point source (Langston, 1975). Since the adsorptive properties of activated carbon depend on its characteristics (pore number and size, surface area, etc.) as well as on temperature, pressure, and rate of flow, it is possible that an activated carbon unit attached to the ventilating system of a plant could adsorb PCBs from the air stream; however, we could not ascertain that such a system is currently in use.

Another device that might remove PCB vapor is a charged droplet scrubber (CDS) such as that produced by TRW. Its effectiveness in controlling emissions of fine particulates has been demonstrated (see Section VI.E.1). In theory, it will also capture PCB vapors and aerosols and, therefore, could be used effectively in ventilating systems, but field testing is needed to confirm its utility (Whitson, 1976).

Control of PCB losses to the atmosphere that result from vaporization of spills and from codistillation is discussed in the sections on the lithosphere (VI.C.2.b.) and the hydrosphere (VI.C.2.c.), respectively.

b. Losses to Lithosphere. The ANSI guidelines (1974) mention control measures such as making provision for containment around all askarel processing areas and the prompt cleanup of spills by absorptive materials or by trapping and pumping.

The steps taken by Monsanto (1973a) exemplify specific control techniques. In the manufacturing area, which may be described as a "concrete bathtub," all drainage is directed to trenches and piping and then to a settling basin; thus all spills are contained and removed. On every shift, all pumps are checked for leakage, drip pans and trays are emptied into scrap PCB drums, and all leaks are reported and documented so that corrections are made and the settling basins are observed. Liquid spills and leaks are promptly cleaned up by absorption.

Recommended adsorption materials include rags, sawdust (ANSI, 1974; Monsanto, 1975b) and adsorbent clay (Monsanto, 1975b). Imbiber polymer beads (Dow Chemical Company) for the cleanup of PCB spills are being marketed by Uedcor Environmental Protection Corporation in the form of beads, bags, and blankets; they can imbibe (adsorb) 27 times their volume and the resultant solid is handled more easily and can be handled and transported without danger of spills and leaks (Taylor, 1975).

Adsorptive materials that are effective in cleaning up PCB spills include activated carbon and urethane foam.

c. Losses to Hydrosphere. ANSI (1974) recommendations specify the establishment of containment provisions to ensure against inadvertent loss of PCBs to sewer systems in the event of spillage, leakage, or other uncontrolled conditions or events. Ideally, all sewer systems and effluent streams that could be contaminated with PCBs should be isolated. This has been achieved at the Monsanto manufacturing facility where all sewers are now above ground and combined (Monsanto, 1975b).

PCB-contaminated water need not be discharged from the plant. General Electric reportedly recycles it or drums it for suitable disposal (Anonymous, 1975b). Carbon adsorption, limestone beds, and solvent extraction are techniques that can be used prior to recycling (ANSI, 197[illegible]).

The problem of PCBs in effluent discharge has been the subject of much attention (e.g., EPA, 1973; Courchaine, 1975; Anonymous, 1975a). Various systems have been devised that do reduce significantly the PCB concentration in effluents.

Once such system is the Calgon Adsorption Service (CAS) of the Calgon Corporation (Lauros, 1975). The Calgon adsorption unit uses granular activated carbon, which has a very high capacity for adsorbing PCBs, i.e., its adsorption efficiency is more than 99 percent for dissolved PCBs. CAS will install, operate, and maintain the unit, guarantee the effectiveness, monitor the effluent, make a monthly report, and exchange the exhausted carbon as needed. Validation studies are now in progress. On the basis of current data, Calgon will guarantee that effluent PCB concentrations will not exceed 500 ppt provided that the equipment is operated properly, the design and operating limitations are not exceeded, and the built-in safety factor is not exceeded. Two such units should be on-line for clients by mid-1975. The exhausted carbon can be incinerated, which destroys PCBs. Alternatively, it can be regenerated in a furnace; this process volatilizes the PCBs which are then led to an afterburner where they are destroyed.

A California-based company, Envirogenics, has developed a system for the iron-catalyzed reduction of organochlorine compounds present in the hydrosphere (Sweeney, 1975). Their system has been successfully applied to a variety of organochlorine pesticides and Velsicol is planning to use the method to control the levels of endrin in the production plant effluents. A pilot program to assess the feasibility of catalytic reduction of PCBs was established in December 1975. The method dechlorinates the PCBs but the exact nature of the products and the extent to which dechlorination occurs is not yet known.

One unnamed PCB polluter has expressed interest in this form of effluent control since it appears as if the cost will be lower than for carbon adsorption type control devices. The reductive dechlorination system should be available commerically by the end of 1976.

The Gedcor Environmental Protection Corporation is experimenting with the Dow imbiber beads (Taylor, 1975) in an attempt to perfect a system that can be used for effluent filtration; at present, their device functions as a safety valve that shuts off flow in the event of a spill.

Although as noted above, there are some promising developments in controlling PCB release to the hydrosphere, apparently no method has yet been devised that can guarantee zero concentration of PCBs in effluent discharge.

D. CONTROL OF PCB LOSSES IN USE

Use of PCBs is currently restricted to the askarels that are used in electrical equipment, primarily in transformers and capacitors. These are closed systems; consequently, the loss of PCBs would occur primarily through leakage, equipment malfunction or failure, and accident.

1. Losses to Atmosphere

The principal source of PCB loss directly to the atmosphere is the leakage from askarel-filled capacitors and transformers which are located atop power poles (Klapp, 1975). The power-factor-correction capacitors of the Forces Command of the U.S. Army that are situated on top of 40-foot power poles are usually dry; i.e., air serves as the insulator. Those which do contain dielectric fluids are old units that hold about one pint (0.47 liter) of askarel each (Klapp, 1975). The pole-mounted power-factor-correction capacitors used by Virginia Electric and Power Company contain about one to two gallons (3.8 to 7.6 liters) of dielectric fluid, which is usually askarel. They are hung in racks, usually in banks of four or five (Lewis, 1976). Pole-mounted distribution transformers contain as much as 50 gallons (189 liters) of askarel, with the amount depending on the size of the transformer (Lewis, 1976).

If the leak is a slow one, the leaking askarel drips or runs down to the ground and the leak might continue for some time before it is noticed. If the unit bursts, the leak is rapid and the askarel would be sprayed out and dispersed over a wide area. Either way, vaporization is more likely from pole-mounted capacitors and transformers because of their location and the droplet form of leakage.

Many capacitors are now being installed in banks of about a dozen within a drip pan (Papageorge, 1975). Although this would prevent direct contamination of the lithosphere, the askarel accumulating in the drip pan would be subject to vaporization, especially since the location atop a power pole would preclude observation and frequent cleanup of any leakage that might occur.

2. Losses to Lithosphere

The control of PCB loss from capacitors atop power poles can be effected by the use of drip pans in which the capacitors are set (Papageorge, 1975) (see Section VI.D.1.). Drip pans could also be placed below pole-mounted transformers to catch and contain any leakage.

On the other hand, pad-mounted surface-level transformers are usually much larger units, and the largest contain more than one thousand gallons (3,785 liters) of askarel (Hall and Haigh, 1974; Hall, 1976). Therefore, in order to prevent PCB contamination of the lithosphere in the event of spills, leaks, or equipment malfunction, it is essential that control measures be applied wherever transformers are used. These controls are of three types: spill prevention, backup measures for containment, and cleanup procedures (Obold, 1975).

Safety valves on transformers shut off the flow of askarel when the equipment malfunctions. One such device that uses imbiber beads (Dow Chemical Company) is distributed by the Gadcor Environmental Protection Corporation. It has been installed on transformers in Dow Chemical Company plants (Taylor, 1975).

To ensure containment within a given area, all floor drains must be sealed, the floor must be impervious, and diking must surround the containment area (Courchaine, 1975; Obold, 1975; Taylor, 1975). An alternative is to place the transformer within a vault.

Should a spill or leakage occur within a contained area, the askarel can be pumped out (Monsanto, 1973b) or cleaned up. Thus, in the Dow Chemical Company plants, imbiber beads or blankets are placed in the containment areas under the transformers. The Salt River Project in Phoenix, Arizona, uses imbiber-bead blankets to clean up spills in contained areas (Taylor, 1975). The various other materials that are used to clean up spills in manufacturing and production facilities (see Section VI.C.2.b) are equally suitable for leaks and spills in other contained areas; these include rags, sawdust, activated carbon, urethane foam, and absorbent clay.

Another source of lithosphere contamination is the runoff from rainwater that washes outdoor transformers (Papageorge, 1975). A Gadcor ecology protection system (Gadcor Environmental Protection

Corporation) is now being installed at the General Motors Cadillac plant in Detroit, Michigan, to solve this problem. There will be a cement base under the transformer and a 12-inch high dike surrounding the area. A 4-inch pipe coupling will pass through the dike, and to it on the outside will be attached an imbiber bead valve (Taylor, 1975). This system will permit the drainage of rainwater and melted snow from the transformer containment area, but PCB contaminant will be stopped by the imbiber bead valve.

There have been at least two accidents with large askarel-containing transformers that resulted in significant contamination of the lithosphere. One occurred when an 800-gallon askarel-containing transformer was dropped while it was being installed in Chicago, Illinois, (Willmore, 1976). The other accident occurred near Kingston, Tennessee, during shipment of a 1400-gallon askarel-containing transformer (Hall and Haigh, 1974; Hall, 1976). Such accidents cannot be completely eliminated. The best method for controlling this type of PCB contamination is rapid, effective, and thorough cleanup of the spill.

The EPA Oil and Hazardous Materials Spills Research Branch in Edison, New Jersey, is now working on a pilot project to determine the feasibility of a shroud for use in cleaning up land spills. It would be rapidly deployable and would be suitable for use with tank cars, transformers, etc. The shroud would have a wet scrubber on one end and be capable of pulling 40,000 cfm. The unit would function as a mixing chamber into which could be added water, activated carbon, ion exchangers, and/or imbiber beads as necessary. The study should be finished about June 1976 (Lafornara, 1975).

3. Losses to Hydrosphere.

Surface runoff of PCB-contaminated rainwater can be prevented by the construction of containment areas around all outdoor transformers. Containment areas for indoor transformers and proper housekeeping procedures will keep askarels out of sewers.

An interesting and unexpected contamination of the hydrosphere occurred when a transformer broke through its packing crate while it was being loaded aboard a barge at the port of Seattle, Washington, (Evans, 1975; Holsinger, 1975). The transformer broke and about 265 gallons (1,003 liters) of askarel spilled in the river (Goff, 1975). The cleanup task was handled by the Regional Response Team from EPA Region 10. Contaminated sediment was transported to the surface by vacuum lines hand-held by divers. The slurry was dewatered by use of alkyl flocculant and settling ponds. The water with suspended solids and PCBs was then pumped through a Rexnord Treatment Unit (a truck-mounted sand-anthracite filter followed by an activated-carbon filter) before it was deemed sufficiently free of PCBs to be returned to the waterway (Goff, 1975; Lafornara, 1975). The PCB concentration decreased during treatment from 400 ppb in the settling ponds to 4 ppb after the sand filtration and 0.4 ppb after filtration through activated carbon. About 90 gallons (340 liters) of askarel were recovered (Blazevich, 1975). The sludge filled one-hundred 150-gallon drums (Goff, 1975). It is estimated that about 50 more gallons of askarel are still recoverable (Blazevich, 1975), and that dredging will yield 50,000 cubic yards (38,220 cubic meters) of PCB-contaminated sediment (Goff, 1975). The rest of the spilled askarel is probably lost to the environment; some penetrated the soil, some migrated upstream with the salt wedge*, some was dispersed throughout the harbor (Blazevich, 1975).

E. CONTROL OF PCB LOSSES IN DISPOSAL

The recommended method of disposal of PCBs and PCB-contaminated liquids and software (e.g., clothing, rags, sawdust) is by high-temperature incineration, whereas contaminated hardware (e.g., transformers) should be solvent-rinsed and buried in a sanitary landfill (ANSI, 1974; U.S. Army Environmental Hygiene Agency, 1975). The disposal services offered by various companies are listed in Table 6.1.

PCBs and PCB-contaminated materials are shipped to disposal facilities. The ANSI (1974) and IEEE (1974) specifications for drum material, construction, and fittings also apply to drums used for waste materials. Gedcor Environmental Protection Corporation is marketing vapor-barrier bags and transport boxes for the handling and shipment of waste askarels; their Burn Box (Hedwin Cubitainer loaded with an appropriate quantity of Dow imbiber beads) seems to be quite suitable for the disposal of liquid askarels. The imbiber beads

---

*A wedge-shaped mass of salt seawater which intrudes into the fresh river water.

TABLE 6.7
FACILITIES AND SERVICES FOR PCB DISPOSAL

Company	Location	Material Handled	Method	Reference
Chem-Trol Pollution Services, Inc.	Model City, N.Y.	Liquids & software hardware	Incineration Burial	
Vector Environmental Protection Corp.*	Westland, Mich.	Liquids	Incineration	Taylor, 1975
General Electric Co.**	Pittsfield, Mass.	Liquids	Incineration in liquid-injection incinerator	Carnes, 1975
Monsanto Industrial Chemicals Co.	St. Louis, Mo.	Liquids	Incineration	Papageorge, 1975
Nuclear Engineering Co.	Sheffield, Ill.	All liquids & solids	Burial in Class I landfill	
Rollins Environmental Services, Inc.	Bridgeport, N.J. Baton Rouge, La. Houston, Tex.	Liquids & software hardware	Incineration	[illegible], 1975; [illegible], 1975
U.S. Army Forces Command***	Army posts	Liquid & solids	Incineration in pathological incinerators	[illegible], 1975

*Vector Environmental Protection Corporation provides shipping containers (Vern Barrel) and disposal services. Actual disposal is handled under contract with a commercial disposal facility (or facilities).

**General Electric Company put this liquid-injection incinerator into operation in 1972; they handle PCBs from other companies, too, but this service is not advertised.

***The pathological incinerators are for use only by the U.S. Army; these are not commercial facilities.

solidify the askarel and consequently there is no danger of spills or leaks during shipment to a disposal facility where the entire unit is incinerated.

Under proper conditions of high temperature incineration, PCBs are broken down. The important conditions are temperature, residence

$$\text{PCBs} \xrightarrow[\text{2-3\% excess } O_2]{\geq 2000^\circ F} CO_2 + H_2O + HCl$$

$$\text{1.5-2.0 seconds}$$

time, and the concentration of excess oxygen in the stack gas. The specific conditions recommended by ANSI (1974) are two seconds at 2000°F with 3 percent excess oxygen or 1.5 seconds at 2700°F with 2 percent excess oxygen. (Scrubbers are needed to remove the HCl.)

It should be noted that the liquid-injection incinerator developed by General Electric and James Zink operates somewhat differently. Waste liquid is injected into the horizontal incinerator cylinder under considerable pressure and it therefore atomizes almost instantly upon injection. Operating conditions are: residence time = 2 to 12 seconds; temperature - 1200 to 1800°F; and excess air - 50 to 100 percent (Bachli, 1975). Because of these modifications, emissions are almost zero (Carnes, 1975). Five test runs were designed to demonstrate the efficiency of the incinerator in destroying DDT. The waste industrial oil burned to provide additional heat was contaminated with approximately 1.7 percent PCB. Therefore, these tests also evaluated the effect of the incineration on PCBs. The destruction efficiency for PCBs ranged from 99.9921 percent to 99.9995 percent, with an average of 99.9956 percent (Leighton and Feldman, 1975). Carnes of the EPA Solid and Hazardous Waste Research Laboratory in Cincinnati, Ohio, commented that this incinerator is a "good and well-operated system, the most efficient incinerator" he has seen (1975).

Lockheed Corporation in Palo Alto, California, is currently engaged in a study on low-temperature plasma destruction for hazardous waste disposal, and PCBs are included in this study. (This project is contracted by USEPA, Solid and Hazardous Waste Research Division, Municipal Environmental Research Laboratory, Cincinnati, Ohio, under EPA contract 68-03-2190, "New Methods for Efficient Detoxification/Destruction of Hazardous Wastes," with Don Oberacher as the EPA Project Officer.) The preliminary findings from this study are promising; the economics are unknown (Carnes, 1975).

1. Losses to Atmosphere

If one assumes that the commercial disposal facilities that handle PCBs do operate properly -- e.g., the Rollins Environmental Services facility in Bridgeport, New Jersey, is certified by the state of New Jersey for waste industrial incineration with no restrictions (Koneval, 1975) -- then these incinerators would not be a source of PCB contamination of the atmosphere. However, most municipal incinerators probably do not operate under the designated conditions that are necessary for PCB destruction. Consequently, they constitute sources of PCBs, especially since they would be handling non-labelled PCBs and PCB-contaminated wastes as well as other PCB-containing products.

In their study of this problem, Carnes et al. (1973) detected PCBs in the residue fines and also in the fly ash from particulate control devices of several municipal incinerators. One fly ash sample (from Media, Pennsylvania) was taken from the bottoms of a clarifier of a wet-wall, baffle-type scrubber; a second sample (from New Orleans, Louisiana) was from the hopper of a multiple cyclone-type collector. Carnes concludes that this finding indicates that: (1) PCBs are heat-resistant; (2) PCBs are probably associated with (have an affinity for) particulates and fly ash; (3) PCBs enter the air in fly ash; (4) an undetermined fraction of PCBs emitted by incinerators is removed by particulate control devices; and (5) PCBs are probably also vaporized and enter the atmosphere in the gas emissions (Carnes, 1975).

Various scrubbers are effective in removing complete and incomplete combustion products from emissions prior to venting from the stacks. These include cyclones, venturi scrubbers, high-energy scrubbers, electrostatic precipitators, and fiber filter bags. Charged droplet scrubber systems (e.g., that manufactured by TRW) effect removal of fine particulates in the micron and submicron size range (TRW, 1975; Lear et al., 1975). In most incinerators, however, the only scrubbing that occurs is when exit gas containing fly ash passes into a baffle system that has water running down the wall (Carnes, 1975).

PCB vapors can probably be removed from the emissions by alkaline scrubbing at pH 11 to pH 12 (Carnes, 1975). Packed-bed scrubbers are also effective in eliminating vapors; the limiting factor is economics.

The absorbent liquid from scrubbers would contain PCBs. This includes the PCBs associated with the particulates that dissolve in the supernatant liquid while the particles are settling in the clarifier as well as the PCB vapor that is scrubbed. Discharge of PCB-containing liquid from scrubbers into ambient waters or even into sewage systems will contaminate the hydrosphere (see Section VI.E.1).

2. Losses to Lithosphere

PCBs can contaminate the lithosphere when they are disposed of improperly. Waste askarel is probably disposed of correctly because of the publication of guidelines for its handling (e.g., ANSI, 1974; U.S. Army Environmental Hygiene Agency, 1975). However, PCB-containing materials are often discarded directly in landfills. In addition, residues and fly ash from incinerators and sludge from waste water treatment plants, which do contain PCBs (Carnes et al., 1973; Hesse, 1975), are usually deposited in landfills.

Proper containers will prevent leaks and spills and also the leaching of PCBs. ANSI (1974) recommends the use of sealed vapor-barrier containers; the instructions of the U.S. Army Environmental Hygiene Agency (1975) specify steel drums and also the inclusion of absorbent material (e.g., vermiculite, sawdust) in the drum when any liquid askarel is present. Whenever possible, all scrap hardware should be drained of askarel and then washed with solvents to remove all traces of PCBs prior to disposal by burial or recycling of the metal(ANSI, 1974).

When burial is the method of disposal, a Class I landfill site should be used. Such a site may accept any type of waste including toxic and hazardous materials because the fill will not enter the groundwater. Class I landfill sites are located in special geologic areas (Baird, 1975) or in special structures such as deep wells (Monsanto, 1975b) or empty missile silos (Goff, 1975). Empty missile silos in southern Idaho were used for disposal of the PCB-contaminated sludge from the Seattle harbor (see Section VI.D.3) (Goff, 1975).

3. Losses to Hydrosphere

PCBs can enter the hydrosphere by runoff of rainwater from improperly disposed-of PCBs and PCB-contaminated materials. Leaching can transfer PCBs from lithosphere to hydrosphere, and PCBs were detected in leachate from landfills (Hesse, 1975). See Section VI.E.2 for a discussion of land disposal methods and landfill sites.

The absorbent liquid from scrubbers that are used to control PCB emissions from incinerators (see Section VI.E.1) is a potential source of PCB contamination of the hydrosphere. Even discharge into sewage systems will not prevent this contamination since municipal waste water treatment plants remove only about 70 percent of influent PCBs with the sludge (Section IV.C.3). Carbon adsorption units now undergoing validation tests by Calgon Corporation can reduce PCB concentration in aqueous effluent to 500 ppt (see Section VI.C.2.c). There are now no control devices that can guarantee zero discharge of PCBs in aqueous effluents.

F. RECOMMENDATIONS IN CONTROL STRATEGIES

The ANSI guidelines (1974), the IEEE guide (1974), and the Monsanto guide (1975b) are the only known publications that pertain to the use of askarels. Although they do contain some discussion of safety and of handling and disposal procedures, the emphasis is on the technical aspects of askarels. There is a definite need for a single publication about the hazards of PCBs. It should include specific recommendations about worker protection; procedures for handling and shipping askarels; techniques for minimizing, containing, and cleaning up spills; and proper methods of disposing of PCBs and PCB-contaminated materials. It should also list the currently available and effective methods, materials, equipment, devices, facilities, and services.

The EPA Oil and Hazardous Materials Spills Research Branch in Edison, New Jersey, is now in the process of developing a manual about PCBs (Lafornara, 1975). This might be the comprehensive manual that is needed.

Once such a manual is available, it should be distributed widely. Monsanto, the United States manufacturer of PCBs, has implemented strict controls in its plants (Monsanto, 1973a). It was impossible to ascertain which, if any, air pollution control measures are being used in consumer industries; General Electric, for example, refers calls about PCBs to an attorney (Babb, 1975). This manual would probably be useful to the consumer industries, and it would certainly be very important to architect and engineering firms for their design work.

1. Losses to Atmosphere

Existing technology is probably sufficient to control PCB losses directly to the atmosphere. The proposed manual should list the devices that effect control for specific situations -- e.g., mist eliminators for ventilating systems, scrubbers for incinerators. It would be difficult to secure compliance with recommendations if there is no legal basis for enforcement.

New technology may eliminate some current sources of PCB contamination. For example, can light-weight economical vaults be devised for enclosing capacitors and/or transformers? Is low-temperature plasma destruction of PCBs feasible, economically as well as technically, and is this method emission-free?

2. Losses to Lithosphere

The problem of leak/spill containment is rather simple. However, clean-up procedures are haphazard. Materials should be studied for suitability, effectiveness, efficiency, availability, and cost-effectiveness. Data from this study should be included in the manual. Alternative clean-up materials and procedures should also be evaluated. The shroud (Section VI.D.2) should be fully evaluated.

3. Losses to Hydrosphere

Although there are some promising developments, apparently there is no technology currently available that can effect and guarantee zero discharge of PCBs from a point-source effluent. Although it is important that PCBs be prevented from entering the industrial sewage, some contamination can and does occur. It is concluded that proper technology be developed to ensure zero PCB concentration in effluent discharge into waterways.

VII. ENVIRONMENTAL EFFECTS OF PCBs

A. SUMMARY

PCBs accumulate in body tissues since they are readily absorbed by inhalation, ingestion, and dermal contact but are not easily metabolized or excreted.

The chronic toxicity of PCB appears to be of greater significance than acute toxicity. The major target organ of PCBs is the liver. Repeated exposures of laboratory animal to low levels of PCBs results in hypertrophy of the liver accompanied by induction of liver microsomal enzyme activity and structural changes in liver cells. Dermatological, gastro-intestinal, hematological, and neural symptoms have been observed in humans and animals exposed to PCBs. PCBs have been implicated as human teratogens. Carcinogenic and embryotoxic effects of PCBs have been observed in laboratory mammals.

B. EFFECTS ON HUMANS AND LABORATORY ANIMALS

1. Absorption and Accumulation

PCBs tend to accumulate in body tissues since they are readily absorbed through ingestion, inhalation, or dermal contact, but they are not easily metabolized or excreted. Although human exposure is mainly through the diet, PCBs will be inhaled wherever they exist in the atmosphere.

Absorption through inhalation has been measured in laboratory mammals. Tombergs (1972) reports a German investigation which found very high absorption in rats after a single inhalation of a mixture of low chlorinated biphenyls. The concentration in body tissues depended on the time since the end of aerosol exposure. Fifteen minutes after exposure, the concentration in the liver reached 50 percent of the maximum concentration attained after two hours (70 μg/g tissue). After 30 minutes, the concentration in fat was 14 μg/g tissue (27 percent of liver concentration at that time) and the concentration in brain tissue was only 9 μg/g tissue (17 percent of liver concentration). Treon et al. (1956) exposed rats, mice, rabbits, guinea pigs, and a cat to PCB vapors five days a week for several weeks. Aroclor 1242 at concentrations of 1.9 and 8.6 μg/l (mg/m^3; the higher number is approximately 1 ppm) had no ill effects. Aroclor 1254 at concentrations of 1.5 and 5.4 mg/m^3 (0.11 and 0.41 ppm) caused enlarged liver in the rats.

Concentrations of PCBs tend to parallel lipid content so that PCB storage in body tissues occurs in the following order (Curley et al., 1971):

Fat > liver > feces > kidney > brain > plasma > urine

The concentration in adipose tissue is 10 to 100 times the concentration found in other tissues both early after single doses (Grant et al., 1971) and after prolonged intake (Curley et al., 1971). PCBs are widely distributed in human adipose tissue. From human adipose tissue studied in their laboratory, Price and Welch (1972) concluded that 41 to 45 percent of the general population have PCB levels of 1.0 ppm or more in their adipose tissue. Yobs (1972) reported results of analyses for PCBs in adipose tissue of the general population of the United States. Of 637 samples analyzed, half were found to contain PCBs. Of these, 198 (31 percent) contained more than 1 ppm but only 33 (5.2 percent) contained more than 2 ppm. Samples were collected from 38 cities in 18 states. Positive samples came from every city sampled. It, therefore, appears that PCBs are widely distributed in human adipose tissue in the United States. Biros et al. (1970) in a qualitative analysis by combined gas chromatography and mass spectrometry (G.C.-M.S.) of two human adipose tissue samples found substantial quantities of PCBs ranging from pentachlorobiphenyls to decachlorobiphenyls. The PCB residues included at least 14 isomers and homologs. Price and Welch (1972) found 10 PCBs in human adipose tissue ranging from hexachlorobiphenyls to nonachlorobiphenyls.

Continuous low level exposure can lead to bioaccumulation of PCBs in fatty tissues of mammals. Even after relatively short term low-level exposures PCBs accumulated in adipose tissue can be retained for a prolonged period. Allen et al. (1974a) fed six adult female rhesus monkeys 25 ppm of Aroclor 1248 for two months. PCB concentrations in samples of adipose tissue averaged 127 µg/g fat for all animals. At that time, the experimental diet was discontinued. Eight months later the PCB content was 34 µg/g fat. Curley et al. (1971) fed Sherman weanling rats a diet containing 100 ppm Aroclor 1254 for 58 days and for 240 days. Animals were sacrificed at various intervals. A steady buildup of PCB in all tissues was observed over the 58 day period. The rats stored more PCB in their tissues after 240 days than at the end of 58 days. In experiments at two dose levels (100 ppm and 500 ppm) for 240 days, Curley et al. (1971) observed that PCB storage was related to the daily dosage. Concentrations of PCB in fat after 240 days at dietary levels of 100 and 500 ppm were 1,101 and 10,021 ppm, respectively. They did not reach a point of equilibrium storage.

When small amounts of PCBs are ingested over an extended period, tissue concentrations may eventually reach toxic proportions. Allen *et al.* (1974a) observed increasing tissue levels for periods in excess of one year when rats were fed a diet containing 100 ppm Aroclor 1248.

Storage of PCBs in body tissues will persist after exposure is terminated. Three years after accidental PCB poisoning, large amounts of PCBs have been found in human adipose tissue (Kuratsune *et al.*, 1971).

Savage *et al.* (1973a; 1973b) found that 20 percent of human milk samples from Colorado mothers contained PCBs with levels ranging from 40 to 100 ppb. Musial *et al.* (1974) found PCBs in all of 15 milk samples from Canadian mothers. Mean PCB concentrations were 20 ppb for whole milk and 1.7 ppm for milk fat. Berglund (1972) reported a mean concentration of 16 ppb in milk from Swedish mothers. These concentrations may be compared with the levels (156-397 ng/g of whole milk) Allen (19[illegible]) found in the milk of rhesus monkeys on PCB-contaminated diets. The nursing monkeys suffered a 30 percent mortality rate.

A nursing infant consumes about 150 g of milk per day per kg of body weight during the second and third months of life (Berglund, 1972). For a PCB level of 16 ppb, this would correspond to 2.4 µg/kg body weight per day. For the range found in 20 percent of milk samples from Colorado mothers, nursing infants would receive 6 to 15 µg/kg/day.

These levels are much greater than the 1 μg per kg per day the U.S. Food and Drug Administration reported as the mean adult human intake from the total diet (U.S. Department of Health, Education and Welfare, 1972b).

2. Metabolism and Elimination

Metabolism of certain components of commercial PCB mixtures is indicated by the frequent observation in gas chromatographic analyses that PCB samples extracted from animals are relatively deficient in early peaks when compared to commercial PCB mixtures. The early peaks are assumed to represent isomers with fewer chlorine atoms. This depletion of lower retention time peaks from tissues of animals fed standard PCB mixtures has been observed in monkeys (Allen *et al.*, 1974a), rats (Curley *et al.*, 1971; Kiriyama *et al.*, 1974; Grant *et al.*, 1971a), and humans (Zitko and Choi, 1971).

Ease of metabolism seems to decrease with increasing chlorine content. Certain structural features such as positional isomerisms can also influence metabolic behavior. Peaks with retention times corresponding to di-, tri-, and tetrachlorobiphenyls are metabolized to the greatest extent. Mammals seem to be able to also metabolize or excrete penta- and hexachloro isomers to some extent (Panel on Hazardous Trace Substances, 1972).

Hydroxylation appears to be the main metabolic route for chlorobiphenyls. These hydroxylated metabolites may then be conjugated with glucuronic acid and excreted into the urine.

Rate of elimination of PCBs from body tissues seems to decrease with an increase in the degree of chlorination. Highly chlorinated biphenyls appear to be hardly eliminated at all since they are not metabolized to excretable forms. The greatest percentage of PCB elimination from body tissues in humans probably occurs through biliary excretion into the gastrointestinal tract (Allen *et al.*, 1974). Very little PCB derived material is found in the urine (Burse *et al.*, 1974).

3. Lethality

Chronic exposure to PCBs poses a greater risk to the general population than acute exposure. Acute LD_{50}[a] in laboratory mammals for a single dose of PCBs can vary from about 2 to 11 g per kg body weight (Interdepartmental Task Force on PCBs, 1972; Grant and Phillips, 1974). Even though toxicity of PCBs is greater when exposures are repeated or continuous, human exposures are unlikely to ever reach lethal levels.

4. Toxic Effects on Liver

The major target organ of PCBs is the liver. Repeated exposures of laboratory animals to low levels of PCBs results in enlargement of the liver accompanied by induction of liver microsomal enzyme activity and structured changes in liver cells.

Among the most readily observed effects is an increase in weight of the liver. Litterst *et al.* (1972) observed increased liver-to-body weight ratios for rats fed diets containing 50 ppm PCBs for four weeks. When rats are maintained on PCB-contaminated diets, liver enlargement is progressive. Allen and Abramson (1973) fed rats diets containing 1000 ppm for six weeks. Increase in liver size became obvious in one day and the liver became larger as the experiment progressed.

---

[a] LD_{50} = that dose of a compound which will produce death in 50% of the animals.

The increase in liver weight is due mainly to proliferation of smooth surfaced membranes of the endoplasmic reticulum, a network of interconnected channels present in the cytoplasm of most animal cells. The endoplasmic reticulum contains complexes of enzymes which play a role in metabolizing foreign substances such as drugs or environmental pollutants. When liver samples are homogenized, the endoplasmic reticulum is broken up into particles referred to as microsomes and the enzymes are often referred to as microsomal enzymes. The liver microsomal enzymes responsible for metabolizing substances not normally expected to be present in the human body are sometimes referred to as drug-metabolizing enzymes. Norback and Allen (1972) observed a proliferation of smooth endoplasmic reticulum (SER) in rats fed PCBs for one to five weeks. Similar proliferation of SER has been observed in mouse and monkey livers (Nishizumi, 1970).

The proliferation of SER is accompanied by increased activity of the microsomal drug-metabolizing enzymes. Disruptions in normal enzyme activity have been observed even at dose levels which had no effect on liver weights or on liver-body weights ratios (Litterst *et al.*, 1972). Chronic exposure to low dose levels of PCB might exact an effect on enzyme activity in human liver (Allen and Abrahamson, 1973; Litterst *et al.*, 1972; Chen *et al.*, 1973). As long as exposure to PCBs continues, induced levels of microsomal enzyme activity persist (Norback and Allen, 1972). After termination of exposure, the enzyme inducing effect of PCBs appears to be reversible. Litterst and Van Loon (1974) maintained rats on a diet of 50 ppm PCB for seven days. Discontinuation of PCB treatment resulted in a slow decay of the induced enzyme activity to approximately control levels after ten days.

Structural changes in liver cells, in addition to proliferated smooth endoplasmic reticulum, include: increase in lipid droplets within the cytoplasm, the formation of numerous multi-layered concentric membrane arrays, increase in numbers of microbodies and lysosomes within cells, and reduction of rough endoplasmic reticulum.

Numerous liver lesions can be observed after exposure to PCBs. Dietary exposure (500 ppm) of Sherman rats to Aroclor 1254 for six to eight months produced extensive areas of adenofibrosis in the liver. Fatty metamorphosis, accumulation of brown pigment in hepatic macrophages,and Kupffer cells are also seen (Kimbrough *et al.*, 1972a; Kimbrough *et al.*, 1973).

3. *Effects on Epithelium*

Dermal effects were among the earliest recognized signs of PCB toxicity. During the 1930s and 1940s, large outbreaks of chloracne occurred in a number of factories manufacturing PCBs or PCB products. Jones and Alden (1936) reported one of the first outbreaks of chloracne occurred in a company that was engaged in manufacture of PCBs. Twenty-three workers had an acne-form eruption on the face and body.

Dermal effects in humans were observed during an outbreak of PCB poisoning in Japan during October 1968. This epidemic was caused by accidentally contaminated rice-bran oil produced by a company in Kitakyusha City and known as K rice oil. Analysis of some of the recovered rice oil showed that it contained from 2000 to 3000 ppm of Kanechlor 400 (Shea, 1973). Kanechlor 400 is a commercial mixture of PCBs containing 48 percent chlorine. The disease became known as "Yusho" or oil disease.

The subjective symptoms of Yusho patients are listed in Table 7.1. Most of these symptoms relate to the skin and eyes (Kuratsune *et al.*, 1972). Dermatological symptoms included acneform eruptions with marked enlargement and elevation of the follicular opening. Increased pigmentation of the skin, lips, gums, nails, and mucous membrane of the oral cavity were noted. Itching of the skin and "stiffening" of the soles of the feet and the palms of the hands were also observed. Cysts formed on the sebaceous glands in the genital region. Other symptoms included dry skin, excessive perspiration, abnormally excessive growth of hair, and swelling of Montgomery's gland in the breast. Many patients were still suffering from the disease after three years of treatment (Kuratsune *et al.*, 1971 and 1972).

Table 7.1 SYMPTOMS OF YUSHO PATIENTS (89 MALES, 100 FEMALES, AS OF OCTOBER 31, 1968)

Symptoms	Males %	Females %
Blackening of nails	83.1	75.0
Distinctive hair follicles	64.0	56.0
Excessive sweating in palms	50.6	55.0
Acnelike skin eruptions	87.6	82.0
Red spots on limbs	20.2	16.0
Itching	42.7	52.0
Change in skin color	75.3	72.0
Swelling of limbs	20.2	41.0
Stiffened soles of feet and palms of hands	24.7	29.0
Pigmentation of mucous membranes	56.2	47.0
Increased eye discharge	88.8	83.0
Hyperemia of mucous membranes in eyes	70.8	71.0
Temporary failing of eyesight	56.2	55.0
Jaundice	11.2	11.0
Swelling of upper eyelids	71.9	74.0
Sense of weakness	58.4	52.0
Numbness of limbs	32.6	39.0
Fever	16.9	19.0
Hearing difficulty	18.0	19.0
Spasms of limbs	7.9	8.0
Headaches	30.3	39.0
Vomiting	23.6	28.0
Diarrhea	19.1	17.0

Source: Kuratsune, Yoshimura, Matsuzaka, and Yamaguchi, 1971. Yusho, a Poisoning Caused by Rice Oil Contaminated with Poly Chlorinated Biphenyls. HSMHA Health Reports 86(12): 1083-1091.

The epithelial tissues of the gastrointestinal tract can be affected by PCBs. Allen and Norback (1973) observed hyperplasia and dysplasia* of the gastric mucosa in subhuman primates fed PCBs for three months. Edematous thickening of the stomach wall and marked hypertrophy** of the pyloric and fundic gastric mucosa occurred. The increased cellularity of the mucous glands with invasion of the muscularis mucosae and accompanying inflammation, observed by Allen and Norback (1973), is histologically described as a hypertrophic gastritis. Ulceration in the gastric mucosa of some animals developed after erosion of the mucosal epithelium or rupture of large mucinous cysts (Allen et al., 1973a). More recently, Allen (1975) observed dermatological symptoms in adult female rhesus monkeys which had been fed diets containing 2.5 and 5.0 ppm of Aroclor 1248 for one year. These monkeys developed swelling surrounding the socket of the eye, loss of hair, areas of diffused redness over the skin, and acneform lesions. These symptoms developed in one to two months at dosage levels equal to or half the FDA temporary tolerance of 5.0 ppm for fish or poultry fat (U.S. Department of Health Education and Welfare 1972a). The same pattern of dermatological symptoms in rhesus monkeys fed low dosage levels of PCBs were also observed by McNulty (1975), who added 3 ppm of Aroclor 1242 to regular monkey chow. Studies by Bell (1976) of the effects of PCBs on gastrointestinal epithelial cells of rhesus monkeys were based on both light and electron microscopic observations.

---

* Dysplasia = abnormal development of tissues.

**Hypertrophy = increase in size of an organ or structure usually not resulting from increase in number of cells.

After ingestion of 100 ppm PCBs for two months, the parietal cells, which secrete hydrochloric acid, and the zymogenic cells, which secrete enzymes, had totally disappeared and had been replaced by mucous-secreting cells. These effects also took place at dose levels of 3, 10, or 30 ppm, but more time elapsed prior to onset of symptoms with the lower dose levels.

The experimental concentration of PCBs (3 ppm) within the entire diet, which was sufficient to produce alteration of the gastrointestinal epithelium in subhuman primates, is far below the levels that have occurred in samples of milk fat (28 ppm) and of fish (35 ppm) (Kolbye, 1973). This concentration is much less than levels that occurred in Japanese rice oil during the Yusho incident (2000 to 3000 ppm) (Kuratsune *et al.*, 1972).

The magnitude of the chronic effects which could be produced in humans by PCB-induced hypertrophic gastritis has not been determined. During the 1968 Japanese rice oil poisoning incident, some PCB poisoned victims developed visceral symptoms without the characteristic dermatological symptoms. Symptoms shown by these patients included nausea, vomiting, colic-like attacks of abdominal pain, and diarrhea (Umeda, 1972). Gastrointestinal symptoms were also seen in more typical "Yusho" cases. Kuratsune *et al.* (1971) reported vomiting in 26 percent and diarrhea in 18 percent of Yusho victims. These symptoms in humans as well as weight loss in humans and animals exposed to PCBs may be related to compromised gastric function. Allen and Norback

(1973) suggest that the increased cellularity, abnormal dysplastic growth pattern, and invasion of adjacent tissue regions might indicate eventual neoplastic transformation.

6. Hematological Effects

Changes in blood composition and bone marrow histology have been observed in humans and animals after exposure to PCBs.

Decreases in hemoglobin and in red blood cell count and increases in leukocytes were observed in the most severe Yusho cases. Total blood serum lipids increased, reflecting mainly an increase in triglycerides. Total serum protein levels and levels of most electrolytes were normal (Kuratsune, 1972). Hirayama *et al.* (1974) found that serum triglyceride concentration correlated with serum levels of PCBs. In follow-up studies four years after the Yusho incident, over half the Yusho patients still showed hypertriglyceridemia.

Allen *et al.* (1973b) found that hematological changes developed gradually in rhesus monkeys fed diets containing 300 ppm Aroclor 1248. Over three months, there was a decrease in hemoglobin of approximately 2 g/100 ml and a decrease in hematocrit[a] from 40 to 33 percent. Allen *et al.* (1974b) speculate that PCBs may have an inhibiting effect on the red-blood-cell-forming tissue of bone marrow.

Hypobilirubinemia, a lowered concentration of serum bilirubin, has been observed in PCB poisoning patients. The serum bilirubin concentration in Yusho patients correlated inversely with blood levels of polychlorinated biphenyls (Hirayama et al., 1974). It is suggested that the hypobilirubinemia in PCB poisoning is caused through either inhibition of heme catabolism or augmentation of bilirubin elimination. It seems more likely, however, that the decrease in concentration of serum bilirubin, a product of heme catabolism, is due to reduced hemoglobin production in PCB-poisoned victims.

---

[a] Hematocrit - The volume of red blood cells packed by centrifugation in a given volume of blood; expressed as percentage of total blood volume which consists of red blood cells.

7. Nervous System Effects

Effects of PCBs on sensory nerves were observed during the 1968 Yusho epidemic in Japan. No symptom was found suggesting involvment of cerebrum, spinal cord,or cranial nerves. Spinal nerve symptoms, however, were present (Murai and Kuroiwa, 1971).

Symptoms suggesting sensory nerve involvement were observed in 10 out of 21 (48 percent) of the Yusho patients studied by Murai and Kuroiwa (1971). These symptoms included numbness, pain, hypoesthesia[*], and areflexia[**]. Slowing of peripheral sensory conduction velocity was also observed in 48 percent of the cases, but motor nerve conduction velocity was not affected except in one case. No patient revealed muscular atrophy or weakness. These data suggest the predominant involvement of the sensory nerves in cases of PCB poisoning in humans (Murai and Kuroiwa, 1971).

---

*Hypoesthesia = dulled sensitivity to touch.
**Areflexia = absence of reflexes.

8. Carcinogenesis

No epidemiological studies indicating a relationship between PCBs and cancer in humans are available. A limited number of bioassays of PCBs have been performed and additional tests for carcinogenicity are being conducted.

Kanechlor 500 and Aroclor 1254 have been shown to be carcinogenic in mice when administered orally. Nagasaki *et al*. (1972) fed male dd[a] mice diets containing Kanechlor 300, 400, or 500 for 32 weeks. Mice fed the diet containing 500 ppm Kanechlor 500 developed hepatocellular carcinomas. All types of Kanechlor produce benign liver tumors in mice (Ito *et al*., 1974). Kimbrough and Linder (1974) fed mice diets containing 300 ppm Aroclor 1254. After 11 months on the diet, 9 out of 22 mice developed hepatomas. All 22 mice developed adenofibrosis.

PCBs appear to have some type of co-carcinogenic activity. Ito *et al*. (1973) found that PCBs have a promoting effect on malignant lesions induced in mouse livers by isomers of benzene hexachloride. Among groups of mice fed benzene hexachloride alone, only the group receiving 250 ppm of the α-isomer developed hepatocellular carcinoma. When the diet was supplemented with PCBs, hepatocellular carcinoma were induced in mice receiving only 50 or 100 ppm α-benzene hexachloride. Diets containing β-benzene hexachloride caused hepatocellular carcinomas only when the diet was supplemented with PCBs.

---

[a] dd = a strain of mice.

Many potential carcinogens require biotransformation by microsomal enzyme systems, of the type induced by PCBs, before they become active carcinogens. On the other hand, metabolism of primary or ultimate carcinogens may reduce their carcinogenic properties (Popper *et al.*, 1973; Vaino, 1974).

9. Teratogenesis and Other Reproductive Effects

PCBs have been implicated as human teratogens. Teratogenesis is the induction of structural or functional development abnormalities by exogenous factors during gestation. Even a substance that is regarded as safe for adults can be harmful to the fetus. The fetus is characterized by an active proliferation of cells. A slight influence on these proliferating cells can produce an abnormal development of the fetal body.

During the Yusho incident in Japan during 1968, damage to newborn infants was observed. Because of dark brown staining of skin and mucous membranes, the infants were referred to as "cola-colored babies." More than 10 cases were reported in the northern part of Kyushu. Many other fetal symptoms were observed, such as stillbirth, substandard birth weight, abnormal pigmentation, desquamation of skin and mucous membranes, abnormally early appearance of teeth, calcification of the skull, wide fontanelles, exophthalmos, and gingival hypertrophy. Intrauterine growth suppression was confirmed in six cases (Funatsu *et al.*, 1972).

Transfer of PCBs from mother to fetus through the placenta was confirmed by demonstrating the presence of PCB in adipose tissue and skin of the stillborn infant (Funatsu *et al.*, 1972). The mothers were sometimes free of clinical disease (Fraumeni, 1976).

In addition to their teratogenic effects, PCBs can cause abortions, stillbirths, and reduced conception rates in laboratory animals. Doses of 12.5, 25.0, and 50 mg/kg/day induced abortions and stillbirths in rabbits when PCBs were administered orally to rabbits during the first 28 days of gestation (Villeneuve *et al.*, 1971). Kato *et al.* (1972) administered doses of 25, 75, 225, and 675 mg/kg/day to rats daily from the first day of pregnancy. Incidence of stillbirth or abortion increased as dose increased. Allen (1976) observed a decrease in live births from adult female monkeys fed low levels of PCBs for six months prior to mating. The rate of conception was only marginally reduced by PCB exposure. In monkeys receiving 5 ppm of PCBs, six conceptions occurred in eight monkeys. All eight monkeys receiving 2.5 ppm of PCBs and all 12 control monkeys conceived. The rates of abortions and resorptions were, however, greatly increased in monkeys receiving PCBs. Four of the six conceptions in the mothers receiving 5 ppm and three of the eight conceptions in mothers receiving 2.5 ppm resulted in abortions or resorptions. These abortions tended to occur early in pregnancy (during the first 45 to 60 days). No abortions or resorptions occurred in control monkeys. All 12 control monkeys had live births. Five of the eight monkeys receiving 2.5 ppm had live births. One live birth and one stillbirth occurred in monkeys receiving 5 ppm PCBs in the diet. Allen (1976) observed a 50 percent mortality rate among the six infants nursing from mothers who continued receiving PCBs in their diet for three to four months after delivery. The infant deaths included the one baby born to a mother receiving 5 ppm and two out of the five babies born to mothers receiving 2.5 ppm. The mothers' milk contained an average of 16.5 µg per gram of milk fat (16.5 ppm). The FDA temporary tolerance for PCBs in milk fat is 2.5 ppm (U.S. Department of Health, Education and Welfare, 1972a).

C. OTHER ENVIRONMENTAL EFFECTS

1. Introduction

Since PCBs are persistent and ubiquitous in the environment, exposure of living things to PCBs is inevitable. Estimation of the effects of PCBs on plants and animals is, however, difficult. The types of adverse effects likely to result from PCB contamination of the environment include histological, biochemical, and reproductive effects. These are all much harder to detect than gross pathological lesions or mortality. Also, rarely is an organism in its natural environment exposed to a single pollutant. When toxic effects are noted, it is therefore difficult to attribute them solely to PCBs.

2. Microorganisms

Some microbial degradation of PCBs may occur in the environment. The ability of bacteria to degrade PCBs depends on the degree of chlorination and structure of the isomer. Mono-, di-, and trichlorinated biphenyls and PCBs with one unsubstituted ring are most readily degraded (Baxter *et al.*, 1975; Ahmed and Focht, 1973).

The effect of PCBs on microbial growth can vary. Differing sensitivities of bacteria to PCBs may cause changes in bacterial community populations. PCBs are inhibitory to phytoplankton,* which have an important role in the ecosystem as primary producers, nutrient cyclers, and oxygen suppliers. Protozoa and plankton also play a role in accumulation and translocation of PCBs to higher trophic levels.

3. Aquatic Organisms

Aquatic organisms accumulate PCBs from water, dietary sources, and sediment. Bioconcentration tends to increase with higher PCB levels in the water, with duration of exposure, with lipid content of organism, and with trophic level. Fish can accumulate 200,000 times more PCBs in their flesh than are found in the surrounding water (Nebeker, 1975). The indirect toxicity of PCBs to predators through accumulation of PCBs in tissues of food organisms may cause deaths from water concentrations that do not cause direct lethality (Nebeker, 1975).

PCBs are toxic to most aquatic organisms. Among aquatic invertebrates, PCBs are toxic to shrimp, crab, snail, and aquatic insect larvae. Molluscs can concentrate and transport PCBs within the marine environment.

At high concentrations, PCBs can be lethal to fish. Juvenile fish are more sensitive than adults (Stalling and Mayer, 1972). Less chlorinated PCBs are more toxic to fish than more highly chlorinated

---

*Phytoplankton - photosynthetic organisms carried passively by water currents.

PCBs (Stalling and Mayer, 1972). At sublethal concentrations, PCBs can cause anemia and metabolic alterations such as hyperglycemia and increased thyroid activity. PCBs decrease activity of ATPases, enzymes associated with osmoregulation[*] (Yap *et al.*, 1971; Cutkomp *et al.*, 1972). Exposure of fish to PCBs can result in decreased egg production, hatching, and survival of fry. Prolonged exposures to very low levels may be more harmful to fish than acute exposures to higher levels (Nebeker, 1975).

PCBs are toxic to freshwater organisms at concentrations below 5 µg/l (ppb) (Nebeker, 1975). Newly hatched fish and small insects and crustaceans with short life cycles are most sensitive. Aroclor 1254 at 0.45 µg/l (ppb) produced a 50 percent decrease in midge reproduction; 1.3 µg/l (ppb) caused a 50 percent reduction in *Daphnia* reproduction; and 1.8 µg/l (ppb) produced 50 percent reduction in fathead minnow reproduction.

Low levels of aroclor 1254 affect reproduction of sheepshead minnows, an estuarine fish (Hansen, 1975). When eggs from adult fish exposed to 0.1 µg/l (ppb) for four weeks were fertilized and placed in PCB-free water, survival of fry was diminished. Mortality of fry increased as PCB content of the eggs increased (Hansen, 1975).

6. Birds

PCBs accumulate in body tissues of birds exposed to PCBs in the environment. PCBs can be lethal to birds depending on level of exposure, degree of chlorination, and sensitivity of the bird. Sensitivity of the bird will depend on its age, sex, and species. The major effects of chronic low-level exposure of birds to PCBs in the environment would probably be reproductive effects. PCBs can exert adverse effects on egg production (Cecil *et al.*, 1973; Dahlgren *et al.*, 1972), embryonic development (Cecil *et al.*, 1974), embryo viability (Chang and Stokstad, 1975), and hatchability (Platanow and Reinhart, 1973; Lillie *et al.*, 1974b).

---

[*] Osmoregulation - the regulation of salt content of body fluids.

In birds, as in other vertebrates, the liver is the prime target organ of PCBs. Increases in liver size (Lillie *et al.*, 1974b; Hurst *et al.*, 1974) are often accompanied by increased lipid content of liver, a decrease in storage of liver vitamin A (Cecil *et al.*, 1973), and increased hepatic microsomal enzyme activity (Bitman *et al.*, 1972).

Porphyria (Strik , 1973a; Vos *et al.*, 1971; Sinclair and Granick, 1974) and chick edema disease (Rehfeld *et al.*, 1971; Vos, 1972) have been attributed to PCBs.

5. Mammalian Wildlife

Where mammalian wildlife is exposed to sufficiently high concentrations of PCBs, they would probably be affected adversely. The significance of PCBs to wild animals depends primarily upon sub-lethal physiological effects. Since PCBs would be expected to affect growth, behavior, and reproduction, the likely consequences would be slow changes in reproduction rates, population sizes, and relative abundance of species. The changes are subtle and difficult to detect.

Fish-eating mammals, such as wetlands mammals, would be especially likely to ingest large amounts of PCBs. Reproductive failure and mortality have been reported in mink fed PCB-contaminated fish from the Great Lakes. Kit mortality, reaching 80 percent, appeared to depend on the percentage of coho salmon in the minks' diet as well as the duration of feeding the salmon-containing diet. Mink rations that contained other species of Great Lakes' fish caused similar reproductive complications, but to a lesser degree (Aulerich *et al.*, 1973). The clinical signs and lesions in mink fed coho salmon were very similar to those observed in mink fed rations containing 30 ppm supplemental PCBs. These symptoms included anorexia, bloody stools, fatty liver, kidney degeneration, and hemorrhagic gastric ulcers. Quantities of PCBs in the body tissues of mink that died on a coho salmon diet were comparable to PCB levels in mink whose diet was supplemented with 30 ppm PCBs (Ringer *et al.*, 1972; Aulerich *et al.*, 1973).

Mink are highly sensitive to PCBs. The LD_{50} of mink for deaths within 48 hours after a single intraperitoneal injection with Aroclors 1221, 1242, and 1254 are 250 to 500 ppm, 500 to 1000 ppm, and 1000 ppm, respectively. The PCB toxicity to mink varied inversely with chlorine content (Aulerich *et al.*, 1973). Feeding mink on diets that contained 10 ppm PCB depressed growth significantly. All mink fed PCB-supplemented diets failed to produce offspring. Mink fed diets supplemented with 10 or 30 ppm failed to produce offspring (Ringer *et al.*, 1972; Aulerich *et al.*, 1973).

Platonow and Karstad (1973) investigated the effects of chronic feeding of low levels of PCBs in mink. No live kits were produced and all adult mink died during a 105-day period of feeding a ration containing 3.6 ppm. At a level of 0.6 ppm, one of 12 mink produced three kits, all of which died during the first day after birth.

6. Role of Trace Contaminants in Toxicity of Commercial PCB Mixtures

The likehood of PCB contamination by toxic impurities has been proposed by many investigators (Vos *et al.*, 1970; Kimbrough, 1972; McNulty, 1975). In 1970, Vos *et al.* reported that Phenoclor, manufactured by Prodelec in France, and Clophen, manufactured by Bayer in Germany, produced a much higher incidence of edema and liver necrosis in cockerels than did aroclor from Monsanto. Analysis revealed the presence of polar impurities (hexa- and heptachloronaphthalenes and tetra- and pentachlorodibenzofurans) in the two European PCB mixtures (Vos *et al.*, 1970). Since chlorinated naphthalenes were shown to be far less toxic than chlorinated dibenzofurans, the increment in toxicity of European PCB mixtures over Aroclors was attributed to chlorinated dibenzofuran contamination (Vos *et al.*, 1970). Until recently, no contaminants had been reported in American commercial PCB mixtures (Aroclors). However, Bowes *et al.* (1975) found tetra-, penta-, and hexachlorinated dibenzofurans in Clophen A60, Phenoclor DP6, and Aroclors 1248, 1254, and 1260. No contaminants were found in Aroclor 1016. The conclusions of Vos *et al.* (1970) were supported by the finding that the Clophen and the Phenoclor, respectively, contained 11 and 17 times the dibenzofuran concentration found in Aroclor 1260.

Because the dibenzofurans are structurally as well as toxicologically similar to the dibenzodioxins, the effects of the compounds have often been compared. Both classes of chlorinated compounds display high levels of toxicity when three to six chlorine atoms are present, causing chloracne, liver damage, and chick edema disease (Kimbrough, 1972). These symptoms are all also characteristic of PCB toxicity. McNulty (1976) reported that 2,3,7,8-tetrachlorodibenzo-p-dioxin caused exactly the same constellation of pathological changes in rhesus monkeys as did PCBs. Since contaminants are present in PCB mixtures at very low levels, if at all, they are not likely to account for the observed toxicity of PCBs. Aroclor 1248 contained 2 ppm dibenzofuran and Aroclor 1260 contained 0.8 ppm (Bowes *et al.*, 1975). Chlorinated dibenzodioxins have never been reported present in commercial PCB mixtures. Experimental data of McNulty (1975) have indicated that 2,3,7,8-tetrachlorodibenzo-p-dioxin is about 10,000 times as toxic as Aroclor 1242 on a per gram basis. Tetrachlorodibenzofurans are about an order of magnitude less toxic than tetrachlorodibenzodioxins (Kimbrough, 1972). If Aroclors are contaminated at levels from 0.8 to 2.0 ppm, there could not be enough dibenzofuran present to account for the effects of the Aroclor.

VIII. REFERENCES

Ahmed, M., and D.D. Focht. 1973. "Degradation of Polychlorinated Biphenyls by Two Species of Achromobacter." Canad. J. Micro 19: 47-52.

Allen, J.R., and L.J. Abrahamson. 1973. "Morphological and Biochemical Changes in the Livers of Rats Fed Polychlorinated Biphenyls." Arch. Environ. Cont. and Tox. 1: 265-280.

Allen, J.R., and D.H. Norback. 1973. "Polychlorinated Biphenyl- and Triphenyl-induced Gastric Mucosal Hyperplasia in Primates." Science 179 (4072): 498-499.

Allen, J. R., L.J. Abrahamson, and D.H. Norback. 1973a. "Biological Changes in Primates Produced by a Polychlorinated Biphenyl and Triphenyl." Federal Proceedings 32(3 Part 1): 735.

Allen, J.R., L.J. Abrahamson, and D.H. Norback. 1973b. "Biological Effects of Polychlorinated Biphenyls and Triphenyls on the Subhuman Primate." Environmental Research 6(3): 344-355.

Allen, J.R., L.A. Carstens, and D.A. Barsotti. 1974a. "Residual Effects of Short-term, Low-level Exposure of Nonhuman Primates to Polychlorinated Biphenyls." Toxicology and Applied Pharmacology 30(3): 440-451.

Allen, J.R., D.H. Norback, and I.C. Hsu. 1974b. "Tissue Modifications in Monkeys as Related to Absorption, Distribution, and Excretion of Polychlorinated Biphenyls." Archives of Environmental Contamination and Toxicology 2(1) 86-95.

Allen, J.R. 1975. Response of the Nonhuman Primate to Polychlorinated Biphenyl Exposure. Federation Proceedings 34(8): 1675-1679.

Allen, J.R. 1976. Personal Communication.

American Conference of Governmental Industrial Hygienists. 1964. "Threshold Limit Values for 1964." AMA Arch. Environ. Health 9: 545.

American Conference of Governmental Industrial Hygienists. 1973. "Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment." ACGIH, Cincinnati, Ohio.

American Industrial Hygiene Association. 1965. "Chlorodiphenyls." Hygiene Guide Series, Jan.-Feb.

American National Standards Insitute. 1974. "Guidelines for Handling and Disposal of Capacitor-and Transformer-Grade Askarels Containing Polychlorinated Biphenyls." ANSI, C107.1-1974. New York.

Anonymous. 1971. "Pollution Cop's Lot Not 'Appy." *Chemical Week*, Apr. 21: 19-20.

Anonymous. 1973. "OECD Recommends Restricted Use of Polychlorinated Biphenyls." *European Chemical News* - March 2: 21.

Anonymous. 1975a. "A fresh fight over PCB pollution." *Business Week*, pp. 30-31, October 6, 1975.

Anonymous, 1975b. "EPA's Schweitzer Claims PCB Use May Be Broader Than Previously Thought." *Toxic Materials News* 2: 137.

Anonymous. 1975c. "Chementator. . ." *Chemical Engineering*, July.

Anonymous. 1975d. "Chemicals Found in Lake Fish: State PCB Ban Urged," *Michigan Out-of-Doors*, July.

Anonymous. 1975e. "PCB Water Maximum of 1 PPT is 'An Appropriate Goal', EPA Says." *Pesticide Chemical News*. September 3- pages 12-13.

Armour, J.A. 1973. "Quantitative Perchlorination of Polychlorinated Biphenyls as a Method for Confirmatory Residue Measurement and Identification." *Journal of the Association of Official Analytical Chemists* 56(4): 987-993.

Armour, J.A., and J.A. Burke. 1970. "Method for Separating Polychlorinated Biphenyls from DDT and Its Analogs". *Journal of the Association of Official Analytical Chemists* 53(4): 761-768.

Arnts, R.R. 1975. U.S. EPA. Personal communication.

Aulerich, R.J., R.K. Ringer, and S. Iwamoto. 1973. "Reproductive Failure and Mortality in Mink Fed on Great Lakes Fish." *Journal of Reproduction and Fertility* 19 (Suppl.): 365-376.

Bachil, W. 1975. General Electric Co., Pittsfield, Massachusetts. Personal communication.

Bailey, S., P.J. Bunyan, and F.R. Fishwick. 1970. "Polychlorinated Biphenyl Residues." *Chemistry and Industry* 22: 705.

Baird, R. 1975. Los Angeles County Sanitation District, Los Angeles, California. Personal communication.

Baxter, R.A., P.E. Gilbert, R.A. Lidgett, J.H. Mainprize, and H.A. Vodden. 1975. "The Degradation of Polychlorinated Biphenyls by Micro-Organisms." The Science of the Total Environment 4(1): 53-61.

Bell, M. 1975. "Ultrastructural Features of Gastric Mucosa and Sebaceous Glands After Ingestion of Aroclor 1242 by Rhesus Monkeys." Presented at National Conference on Polychlorinated Biphenyls, Chicago, Illinois, November 19-21.

Berglund, F. 1972. "Levels of Polychlorinated Biphenyls in Foods in Sweden." Environmental Health Perspectives Exp 1: 67-71.

Bevenue, A., J.N. Ogata, and J.W. Hylin. 1972. "Organochlorine Pesticides in Rainwater, Oahu, Hawaii, 1971-1972." Bulletin of Environmental Contamination of Toxicology 8(4): 238-241.

Bidleman, T.F., and C.E. Olney. 1974a. "Chlorinated Hydrocarbons in the Sargasso Sea Atmosphere and Surface Water." Science 183(4124): 516-518. 2nd Copy.

Bidleman, T.F., and C.E. Olney. 1974b. "High-Volume Collection of Atmospheric Polychlorinated Biphenyls." Bulletin of Environmental Contamination and Toxicology 11(5): 442-450.

Biros, F.J., A.C. Walker, and A. Medbery. 1970. "Polychlorinated Biphenyls in Human Adipose Tissue." Bulletin of Environmental Contamination and Toxicology 5(4): 317-323.

Bitman, J., H.C. Cecil, and S.J. Harris. 1972. "Biological Effects of Polychlorinated Biphenyls in Rats and Quail." Environmental Health Perspectives Exp. 1: 145-159.

Blazevich, J. 1975. EPA, Seattle, Washington. Personal communication.

Bowes, G.W., M.J. Mulvihill, B.R.T. Simoneit, A.L. Burlingame, and R.W. Risebrough. 1975. "Identification of Chlorinated Dibenzofurans in American Polychlorinated Biphenyls." Nature 256 (7/25): 305-307.

Burse, V.W., R.D. Kimbrough, E.C. Villanueva, R.W. Jennings, R.E. Linder, and G.W. Sovocool. 1974. "Polychlorinated Biphenyls. Storage, Distribution, Excretion, and Recovery: Liver Morphology After Prolonged Dietary Ingestion." Archives of Environmental Health 29(6): 301-307.

Carey, A.E., G.B. Wiersma, H. Tai, and W.G. Mitchell. 1973. "Organochlorine Pesticide Residues in Soil and Crops of the Corn Belt Region, United States-1970." Pesticides Monitoring Journal 6(4): 369-376. 2nd Copy.

Carnes, R.A. 1975. EPA, Cincinnati, Ohio. Personal communication.

Carnes, R.A., J.U. Doerger, and H.L. Sparks. 1973. "Polychlorinated Biphenyls in Solid Waste and Solid-Waste-Related Materials." Archives of Environmental Contamination and Toxicology 1(1): 27-35.

Cecil, H.C., S.J. Harris, J. Bitman, and G.F. Fries. 1973. "Polychlorinated Biphenyl-Induced Decrease in Liver Vitamin A in Japanese Quail and Rats." Bulletin of Environmental Contamination and Toxicology 9(3): 179-185.

Cecil, H.C., J. Bitman, R.J. Lillie, G.F. Fries, and J. Verrett. 1974. "Embryotoxic and Teratogenic Effects in Unhatched Fertile Eggs from Hens Fed Polychlorinated Biphenyls (PCBs)." Bulletin of Environmental Contamination and Toxicology 11(6): 489-495.

Chang, E.S., and E.L.R. Stokstad. 1975. "Effect of Chlorinated Hydrocarbons on Shell Gland Carbonic Anhydrase and Egg Shell Thickness in Japanese Quail." Poultry Science 54: 3-10.

Chen, P.R., H.M. Mehendale, and L. Fishbein. 1973. "Effect of Two Isomeric Tetrachlorobiphenyls on Rats and Their Hepatic Enzymes." Archives of Environmental Contamination and Toxicology 1(1): 36-47.

Choi, P.S.K., H. Nack, and J.E. Flinn. 1974. "Distribution of Polychlorinated Biphenyls in an Aerated Biological Oxidation Wastewater Treatment System." Bulletin of Environmental Contamination and Toxicology 11(1): 12-17.

Compton, B., and J. Bjorkland. 1972. "Design of a High Volume Sampler for Airborne Pesticide Collection." (021-Pesticide Chem.) 163rd Meeting, Division of Pesticide Chemistry, ACS, Boston, Massachusetts.

Courchaine, R.J. 1975. Dear Sir letter to Michigan industries.

Cowherd, C., Jr., M. Marcus, C.M. Guenther, and J.L. Spigarelli. 1975. "Hazardous Emission Characterization of Utility Boilers." EPA-650/2-75-066.

Crosby, D.G., and K.W. Moilanen. 1973. "Photodecomposition of Chlorinated Biphenyls and Dibenzofurans." Bulletin of Environmental Contamination and Toxicology 10: 372-377.

Crosby, D.G., K.W. Moilanen, and A.S. Wong. 1973. "Environmental Generation and Degradation of Dibenzodioxins and Dibenzofurans." Environmental Health Perspectives Exp. 5: 259-266.

Crump-Wiesner, H.J., H.R. Feltz, and M.L. Yates. 1974. "Pesticides in Water: A Study of the Distribution of Polychlorinated Biphenyls in the Aquatic Environment." Pesticides Monitoring Journal 8(3): 157-161.

Curley, A., V.W. Burse, and M.E. Grim. 1973. "Polychlorinated Biphenyls: Evidence of Transplacental Passage in the Sherman Rat." Food and Cosmetics Toxicology 11: 471-476.

Cutkomp, L.K., H.H. Yap, D. Desaiah, and R.B. Koch. 1972. "The Sensitivity of Fish ATPases to Polychlorinated Biphenyls." Environmental Health Perspectives Exp. 1: 165-168.

Dahlgren, R.B., R.J. Bury, R.L. Linder, and R.F. Reidinger, Jr. 1972. "Residue Levels and Histopathology in Pheasants Given Polychlorinated Biphenyls." Journal of Wildlife Management 36(2): 524-533.

Dube, D.J., G.D. Veith, and G.F. Lee. 1974. "Polychlorinated Biphenyls in Treatment Plant Effluents." Journal Water Pollution Control Federation 46(5): 966-972.

Duce, R.A., J.G. Quinn, C.E. Olney, S.R. Piotrowicz, B.J. Ray, and T.L. Wade. 1972. "Enrichment of Heavy Metals and Organic Compounds in the Surface Microlayer of Narragansett Bay, Rhode Island." Science 176(4031): 161-163.

Duke, T.W., J.I. Lowe, and A.J. Wilson, Jr. 1970. "A Polychlorinated Biphenyl (Aroclor 1254) in the Water, Sediment, and Biota of Escambia Bay, Florida." Bulletin of Environmental Contamination and Toxicology 5(2): 171-180.

Durfee, R.L. 1975. "Production and Usage of PCBs in the United States." Paper Presented at the National Conference on Polychlorinated Biphenyls Nov. 19-21, Chicago.

Edwards, R. 1971. "Polychlorinated Biphenyls, Their Occurrence and Significance: A Review." Chemistry and Industry (No Volume) Issue 47: 1340-8 (21 November 71)

Eichelberger, J. 1971. "Persistence of Aroclors in Surface Waters." PCB Newsletter 1: 8-9. U.S. Environmental Protection Agency; National Water Quality Laboratory, Duluth, Minnesota.

Enos, H.F., 1976. Personal communication. U.S. Environmental Protection Agency.

Enos, H.F., J.F. Thompson, J.B. Mann, and R.F. Moseman. April 1972. "Determination of Pesticide Residues in Air" (022-Pesticide Chem.) Division of Pesticide Chemistry, 163rd Meeting; ACS, Boston, Massachusetts.

Evans, T. 1975. U.S. Army, Washington, D.C. Personal communication.

Fishbein, L. 1976. Chromatography of Environmental Hazards. Volume 2-Metals, Gaseous and Industrial Pollutants, Chapter 24-"Polychlorinated Biphenyls." 529-577. North-Holland, American Elsevier.

Fraumeni, J.F. 1974. "Chemicals in Human Teratogenesis and Transplacental Carcinogenesis." Pediatrics 53(5): 807-812.

Funatsu, H., F. Hamashita, Y. Ito, S. Tsugawa, T. Funatsu, T. Yoshikane, and M. Hayashi. 1972. "Polychlorobiphenyl (PCB) Induced Fetopathy. I. Clinical Observation." The Kurume Medical Journal 19(1): 43-51.

Gaffney, P.E. 1974. "PCBs: Another Source?" Science 183 (4123): 367-368.

Garrison, A.W., L.H. Keith and A.L. Alford 1972. "Confirmation of Pesticide Residues by Mass Spectrometry and NMR Techniques." in Fate of Organic Pesticides in the Aquatic Environment: 26-54 Advances in Chemistry Series 111. American Chemical Society, Washington D.C.

General Motors Corporation. 1974. Energy Management Bulletin EM 74-6. November 27.

Goff, G. 1975. U.S. Army, Alexandria, Virginia. Personal communication.

Grant, D.L., W.E.J. Phillips, and G.V. Villeneuve. 1971. "Metabolism of a Polychlorinated Biphenyl (Aroclor 1254) Mixture in the Rat." Bulletin of Environmental Contamination and Toxicology 6(2): 102-112.

Grant, D.L., and W.E.J. Phillips. 1974. "The Effect of Age and Sex on the Toxicity of Aroclor 1254, a Polychlorinated Biphenyl, in the Rat." Bulletin of Environmental Contamination and Toxicology 12(2): 145-152.

Greichus, Y.A., A. Greichus, and R.J. Emerick. 1973. "Insecticides, Polychlorinated Biphenyls and Mercury in Wild Cormorants, Pelicans, Their Eggs, Food and Environment." Bulletin of Environmental Contamination of Toxicology 9(6): 321-328. 2nd Copy. Original Inhouse.

Gustafson, C.G. 1970. "PCBs - Prevalent and Persistent." Environmental Science and Technology 4(10): 814-819.

Hall, R.H. 1976. Dow Chemical Company, Midland, Michigan. Personal communication.

Hall, R.H., and D.H. Haigh. 1974. "Imbiber Beads that Soak Up Oil Spills." The Mangineer 1(2): 5-8.

Hansen, D.J. 1975. "PCBs: Effects on and Accumulation by Estuarine Organisms." Presented at National Conference on Polychlorinated Biphenyls, Chicago, Illinois. November 19-21.

Haque, R., and D.W. Schmedding. 1975. "A Method of Measuring the Water Solubility of Hydrophobic Chemicals: Solubility of Five Polychlorinated Biphenyls." Bulletin of Environmental Contamination and Toxicology 14: 13-18.

Haque, R., D.W. Schmedding, and V.H. Freed. 1974. "Aqueous Solubility, Adsorption, and Vapor Behavior of Polychlorinated Biphenyl Aroclor 1254." Environmental Science and Technology 8(2): 139-142.

Harvey, G.R., W.G. Steinhauer, and J.M. Teal. 1973. "Polychlorobiphenyls in North Atlantic Ocean Water." Science 180 (4086): 643-644.

Harvey, G.R., H.P. Miklas, V.T. Bowen, and W.G. Steinhauer. 1974a. "Observations on the Distribution of Chlorinated Hydrocarbons in Atlantic Ocean Organisms." Journal of Marine Research 32(2): 103-118.

Harvey, G.R., W.G. Steinhauer, and H.P. Miklas. 1974b. "Decline of PCB Concentrations in North Atlantic Surface Water. Nature 252: 387-388.

Harvey, G.R., and W.G. Steinhauer. 1974. "Atmospheric Transport of Polychlorobiphenyls to the North Atlantic." Atmospheric Environment 8(8): 777-782.

Harvey, G.R., and W.G. Steinhauer. 1975. "Harvey and Steinhauer Reply." Nature 256: 249-250.

Hendrickson, E.R. 1968. "Air Sampling and Quantity Measurement." in Air Pollution II. Second Edition, Academic Press New York and London.

Hesse, J.L. 1975. "Polychlorinated Biphenyl Usage and Sources of Loss to the Environment in Michigan." Presented at the National Conference on Polychlorinated Biphenyls: PCBs in the Environment - 1975. Chicago, Illinois, November 19-21.

Hirayama, C., M. Okumura, J. Nagai, and Y. Masuda. 1974. "Hypobilirubinemia in Patients with Polychlorinated Biphenyls Poisoning." Clinica Chemica Acta 55(1): 97-100.

Hochheiser, S. 1976. "State of the Art of Measurement Techniques for Monitoring of Polychlorinated Biphenyls in the Atmosphere." U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory. Research Triangle Park, N.C.

Holden, A.V. 1970. "Source of Polychlorinated Biphenyl Contamination in the Marine Environment." Nature 228(5277): 1220-1221.

Hoisinger, J. 1975. U.S. Army, Fort Lee, Virginia. Personal communication.

Hom, W., Risebrough, A. Soutar, and D.R. Young. 1974. "Deposition of DDE and Polychlorinated Biphenyls in Dated Sediments of the Santa Barbara Basin." Science 184(4142): 1197-1199.

Hubbard, H.L. 1964. "Chlorinated Biphenyl and Related Compounds." Encyclopedia of Chemical Technology, 2nd Edition 5: 289-297.

Hurst, J.G., W.S. Newcomer, and J.A. Morrison. 1974. "Some Effects of DDT, Toxaphene and Polychlorinated Biphenyl on Thyroid Function in Bobwhite Quail." Poultry Science 53(1): 125-133.

Hutzinger, O., and S. Safe. 1972. "A General Method for the Preparation of Tritiated Polychlorobiphenyls of High Specific Activity: 2,2', 5,5'-Tetrachlorobiphenyl-[^{3}H]D and 2,2', 4,4', 5,5'-Hexachlorobiphenyl-[^{3}H]^1." Bulletin of Environmental Contamination and Toxicology 7(6): 374-375.

Hutzinger, O.S. Safe, B.R. Wetzell, and V. Zitko. 1973. "Photochemical Degradation of Di- and Octachlorodibenzofuran." Environmental Health Perspectives Exp. 5: 267-270.

Hutzinger, O., W.D. Jamieson, S. Safe, L. Paulmann, and R. Ammon. 1974a. "Identification of Metabolic Dechlorination of Highly Chlorinated Biphenyl in Rabbit." Nature 252(12/20-27): 698-699.

Hutzinger, O., S. Safe, and V. Zitko. 1974. "The Chemistry of PCBs." CRC Press, Cleveland, Ohio.

Institute of Electrical and Electronics Engineers. 1974. "IEEE Guide for Acceptance and Maintenance of Transformer Askarel in Equipment." IEEE standard 76-1974. IEEE, New York.

Interdepartmental Task Force on PCBs. 1972. "Polychlorinated Biphenyls and the Environment." COM-72-10419. 1-192. National Technical Information Service, Springfield, Virginia (U.S. Dept. of Agriculture, Commerce, Health-Education and Welfare, EPA, and other agencies.

Ito, N., H. Nagasaki, M. Arai, S. Makiura, S. Sugihara, and K. Hirao. 1973. "Histopathologic Studies on Liver Tumorigenesis Induced in Mice by Technical Polychlorinated Biphenyls and Its Promoting Effect on Liver Tumors Induced by Benzene Hexachloride." Journal of the National Cancer Institute 51(5): 1637-1646.

Ito, N., H. Nagasaki, S. Makiura, and M. Arai. 1974. "Histopathological Studies on Liver Tumorigenesis in Rats Treated with Polychlorinated Biphenyls." Gann 65: 545-549.

Jensen, S. 1972. "The PCB Story." AMBIO 1(4): 123-131.

Jensen, S., L. Renberg, and M. Olsson. 1972. "PCB Contamination from Boat Bottom Paint and Levels of PCB in Plankton Outside a Polluted Area." Nature 240: 358-360.

Jones, J.W., and H.S. Alden. 1936. "An Acneform Dermatergosis." Archives of Dermatology and Syphilology 33: 1022-1034.

Kato, T., M. Yabushiti, H. Tuda, A. Arima, K. Takahashi, M. Shimomura, H. Miyahara, M. Adachi, Y. Tashiro, and H. Matsumoto. 1972. "Polychlorobiphenyls (PCB) Induced Fetopathy. II. Experimental Studies: Possible Placental Transfer of Polychlorobiphenyls in Rats." The Kurume Medical Journal 19(1): 53-59.

Kimbrough, R.D. 1972. "Toxicity of Chlorinated Hydrocarbons and Related Compounds." Archives of Environmental Health 25(2): 125-131.

Kimbrough, R.D., R.E. Linder, and T.B. Gaines. 1972. "Morphological Changes in Livers of Rats Fed Polychlorinated Biphenyls." Archives of Environmental Health 25(5): 354-364.

Kimbrough, R.D., R.E. Linder, V.W. Burse, and R.W. Jennings. 1973. "Adenofibrosis in the Rat Liver." Archives of Environmental Health 27: 390-395.

Kimbrough, R.D., and R.E. Linder. 1974. "The Induction of Adenofibrosis and Hepatomas of the Liver in Mice of the BALB/cJ Strain by Polychlorinated Biphenyls (Aroclor 1254)." Journal of the National Cancer Institute.

Kiriyama, S., M. Banjo, and H. Matsushima. 1974. "A Failure to Prevent Absorption of Polychlorinated Biphenyls by Concurrent Feeding of Konjac Mannan in the Rats." Nutrition Reports International 10(3): 151-162.

Klapp, F.J. 1975. U.S. Army, Fort McPherson, Georgia. Personal communication.

Kleinert, S. 1975 Wisconsin Dept. of Natural Resources. Personal communication.

Kolbye, A.C. 1972. "Food Exposures to Polychlorinated Biphenyls." Environmental Health Perspectives Exp. 1: 85-88.

Koneval, L. 1975. Rollins Environmental Services, Bridgeport, New Jersey. Personal communication.

Kopp, T. 1975. U.S. Environmental Protection Agency. Personal communication.

Kuratsune, M., T. Yoshimura, J. Matsuzaka, and A. Yamaguchi. 1971. "Yusho, a Poisoning Caused by Rice Oil Contaminated with Polychlorinated Biphenyls." HSMHA Health Reports 86(12): 1083-1091.

Kuratsune, M.T. Yoshimura, J. Matsuzaka, and A. Yamaguchi. 1972. "Epidemiologic Study on Yusho, a Poisoning Caused by Ingestion of Rice Oil Contaminated with a Commercial Brand of Polychlorinated Biphenyls." Environmental Health Perspectives Exp 1: 119-128.

Kutz, F.W., and H.S.C. Yang. 1975. "A Note on Polychlorinated Biphenyls in Air." Presented at The National Conference of Polychlorinated Biphenyls, Nov. 19-21, 1975, Chicago, Illinois.

Lafornara, J. 1975. EPA, Edison, New Jersey. Personal communication.

Langston, P.B. 1975. Calgon Corporation, Pittsburgh, Pennsylvania. Personal communication.

Law, L.M., and D.F. Goerlitz. 1974. "Selected Chlorinated Hydrocarbons in Bottom Material from Streams Tributary to San Francisco Bay." Pesticides Monitoring Journal 8(1): 33-36.

Lear, C.W., W.F. Krieve, and E. Cohen. 1975. "Charged Droplet Scrubbing for Fine Particle Control." Journal of the Air Pollution Control Association 25: 184-189.

Leighton, I.W., and J.B. Feldman. 1975. "Demonstration Test Burn of DDT in General Electric's Liquid Injection Incineration." USEPA, Region I, Boston, Massachusetts.

Levitz, N, W. Podolski, and E. Carls. Undated. 'Control Technology for Polychlorinated Biphenyls (PCBs)." U.S. Environmental Protection Agency, unpublished contract report.

Lewis, R.V., 1976. Virginia Electric and Power Company, Richmond, Virginia. Personal communication.

Lillie, R.J., S.J. Harris, H.C. Cecil, and J. Bitman. 1974. "Normal Reproductive Performance of Mature Cockerels Fed Aroclor 1248." Poultry Science 53(4): 1666-1667.

Lister, R.E., and R.I.M. Bennett. 1972. "PCBs in Copying Paper." Nature 237(6/16): 516.

Litterst, C.L., T.M. Farber, A.M. Baker, and E.J. van Loon. 1972. "Effect of Polychlorinated Biphenyls on Hepatic Microsomal Enzymes in the Rat." Toxicology and Applied Pharmacology 23(1): 112-122.

Litterst, C.L., and E.J. van Loon. 1974. "Time-Course of Induction of Microsomal Enzymes Following Treatment with Polychlorinated Biphenyl." Bulletin of Environmental Contamination and Toxicology 11(3): 206-212.

Lukey, D. 1975. U.S. Environmental Protection Agency. Personal communication.

Longhurst, A.R., and D.J. Radford. 1975. "PCB Concentration in North Atlantic Surface Water." Nature 256: 239.

Lourca, B. 1975. Calgon Corporation, Pittsburgh, Pennsylvania. Personal communication.

Lunde, G., J. Gether, and B. Josefsson. 1975. "The Sum of Chlorinated and of Brominated Non-Polar Hydrocarbons in Water." Bulletin of Environmental Contamination and Toxicology 13(6): 655-661.

Mackay, D., and A.W. Wolkoff. 1973. "Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmosphere." Environmental Science and Technology 7(7): 611-614.

Martell, J.M., D.A. Rickert, and F.R. Siegel. 1975. "PCBs in Suburban Watershed, Reston, Virginia." Environmental Science and Technology 9: 872-875.

Mason, T. 1975. "Local Chemists Find Safeguards, Replacements For Contaminant." Midland Daily News, June.

Maugh, T.H., II. 1973. "DDT: An Unrecognized Source of Polychlorinated Biphenyls." Science 180 (4086): 578-579.

McNulty, W.P. 1975. Paper presented at National Conference on Polychlorinated Biphenyls, Chicago, Illinois, November 19-21.

McStrack, D. 1975. McGraw Edison. Personal communication.

Monsanto Industrial Chemical Company. Undated. "Aroclor Plasticizers." Monsanto Technical Bulletin O/PL-306A.

Monsanto Industrial Chemicals Company. 1970. "Monsanto Cites Actions Taken on Environmental Issue." (News release - E.V. John, Public Relations Dept).

Monsanto Industrial Chemicals Company. 1972. "Presentation to the Interdepartmental Task Force on PCBs." Washington, D.C.

Monsanto Industrial Chemical Company. 1973a. "Polychlorinated Biphenyl (PCB)." A Presentation to the Effluent Standards and Water Quality Information Advisory Committee, November 29, 1973.

Monsanto Industrial Chemical Company. 1973b. Letter to Dr. Martha Sager, July 13.

Monsanto Industrial Chemicals Company. 1974a. "PCB Manufacture and Sales-Monsanto Industrial Chemicals Company - 1957 Thru 1964." (unpublished data).

Monsanto Industrial Chemicals Company. 1974b. "PCB Manufacture and Sales-Monsanto Industrial Chemicals Company - 1965 Thru 1974." (unpublished data).

Monsanto Industrial Chemicals Company. 1974c. "Proposed Toxic Pollutant Effluent Standards for Aldrin-Dieldrin, Et Al-FWPCA (307) - Docket No. 1." Sworn statement by W.B. Papageorge. St. Louis, Missouri, 14 March 1974.

Monsanto Industrial Chemical Company. 1975a. "A Comparison of Proposed Specifications for Aroclor 1016 with Current Specifications for Aroclor 1242." (unpublished data).

Monsanto Industrial Chemical Company. 1975b. "Transformer Askarel Inspection and Maintenance Guide." Bulletin IC/FF-38B.

Murai, Y., and Y. Kuroiwa. 1971. "Peripheral Neuropathy in Chlorobiphenyl Poisoning." Neurology 21(11): 1173-1176.

Musial, C.J., O. Hutzinger, V. Zitko, and J. Crocker. 1974. "Presence of PCB, DDE, and DDT in Human Milk in the Provinces of New Brunswick and Nova Scotia, Canada." Bulletin of Environmental Contamination and Toxicology 12(3): 258-267.

Nagasaki, H., S. Tomii, T. Mega, M. Marugami, and I. Nobuyuki. 1972. "Hepatocarcinogenicity of Polychlorinated Biphenyls in Mice." GANN 63(6): 805.

Nebeker, A.V. 1975."Summary of Recent Information Regarding Effects of PCBs on Freshwater Organisms." Presented at National Conference on Polychlorinated Biphenyls, Chicago, Illinois, November 19-21.

Nisbet, I.C.T., and A.F. Sarofim. 1972. "Rates and Routes of Transport of PCBs in the Environment." Environmental Health Perspectives Exp 1: 21-38.

Nishizumi, M. 1970. "Light and Electron Microscope Study of Chlorobiphenyl Poisoning--in Mouse and Monkey Liver." Archives of Environmental Health 21(11): 620-632.

Norback, D.H., and J.R. Allen. 1972. "Chlorinated Aromatic Hydrocarbon Induced Modifications of the Hepatic Endoplasmic Reticulum: Concentric Membrane Arrays." Environmental Health Perspectives Exp 1: 137-143.

Oheid, C. 1975. Gilbert Associates, Reading, Pennsylvania. Personal communication.

OECD. 1973. "Polychlorinated Biphenyls: Their Use and Control." Environment Directorate from the Organization for Economic Cooperation and Development. 02066. Paris.

Oloffs, P.C., L.J. Albright, and S.Y. Szeto. 1972. "Fate and Behavior of Five Chlorinated Hydrocarbons in Three Natural Waters." Canadian Journal of Microbiology 18(9): 1393-1398.

Oloffs, P.C., L.J. Albright, and S.Y. Szeto, and J. Lau. 1973. "Factors Affecting the Behavior of Five Chlorinated Hydrocarbons in Two Natural Waters and Their Sediments." Journal of Fisheries Research Board of Canada 30(11): 1619-1623.

Panel on Hazardous Trace Substances. 1972. "Polychlorinated Biphenyls-Environmental Impact." Environmental Research 5(3): 249-362.

Papageorge, W.B. 1975. Monsanto, St. Louis, Missouri. Personal communication.

Peel, D.A. 1975. "Organochlorine Residues in Antarctic Snow." Nature 254 (3/27): 324-325.

Persson, B. 1971. "Chlorinated Hydrocarbons and Reproduction of a South Swedish Population of Whitethroat Sylvia Communis." Oikos 22(2): 248-255.

Platonow, N.S., and L.H. Karstad. 1973. "Dietary Effects of Polychlorinated Biphenyls on Mink." Canadian Journal of Comparative Medicine 37(4): 391-400.

Platonow, N.S., and H.S. Reinhart. 1973. "The Effects of Polychlorinated Biphenyls (Aroclor 1254) on Chicken Egg Production, Fertility and Hatchability." Canadian Journal of Comparative Medicine 37(4): 341-346.

Popper, H., P. Czygan, H. Greim, F. Schaffner, and A.J. Garro. 1973. "Mutagenicity of Primary and Secondary Carcinogens Altered by Normal and Induced Hepatic Microsomes." Society for Experimental Biology and Medicine Proceedings 142(3): 727-729.

Price, H.A., and R.L. Welch. 1972. "Occurrence of Polychlorinated Biphenyls in Humans." Environmental Health Perspectives Exp. 1:73-78.

Rabb, E.L. 1975. General Electric Company, Pittsfield, Massachusetts. Personal communication.

Rehfeld, B.M., R.L. Bradley, Jr., and M.L. Sunde. 1971. "Toxicity Studies on Polychlorinated Biphenyls in the Chick. (1) Toxicity and Symptoms." Poultry Science 50(4): 1090-1096.

Richardson, A.F. 1975. "PCBs are Found in More Waterways; New Curbs Planned." Chemical Marketing Reporter 208(12): 5-20.

Richel, S.M. 1974. "40 CFR 129 (Subpart I)." Letters of January 15 to Hearing Clerk, U.S. Environmental Protection Agency, from General Electric Company, Schenectady, New York.

Ringer, R.K., R.J. Aulerich, and M. Zabik. 1972. "Effect of Dietary Polychlorinated Biphenyls on Growth and Reproduction of Mink." Preprint of paper presented before American Chemical Society, New York, New York, August 27-September 1, 1972. Vol. 12(1): 149-154.

Risebrough, R.W., P. Rieche, D.B. Peakall, S.G. Herman, and M.N. Kirven. 1968. "Polychlorinated Biphenyls in the Global Ecosystem." Nature 220 (12/14): 1098-1102.

Risebrough, R.W., and B. deLappe. 1972. "Accumulation of Polychlorinated Biphenyls in Ecosystems." Environmental Health Perspectives Exp. 1: 39-45.

Ruopp, D.J. and V.J. DeCarlo. 1975. "Environmental Levels of PCBs." Personal communication from D. Lukey, U.S. EPA.

Ruzo, L.O., M.J. Zabik, and R.D. Schuetz. 1974. "Photochemistry of Bioactive Compounds: Photoproducts and Kinetics of Polychlorinated Biphenyls." Journal of Agriculture and Food Chemistry 22: 199-202.

Safe, S., and O. Hutzinger. 1971. "Polychlorinated Biphenyls: Photolysis of 2,4,6,2',4',6'-Hexachlorobiphenyl." Nature 232 (5313): 50-52.

Savage, E.P., J.D. Tessari, and J.W. Malberg. 1973. "The Occurrence of Polychlorinated Biphenyls (PCBs) in Silage Stored in Pit and Upright Silos." Bulletin of Environmental Contamination and Toxicology 10(2): 97-100.

Savage, E.P., J.D. Tessari, J.W. Malberg, H.W. Wheeler, and J.R. Bagby. 1973a. "A Search for Polychlorinated Biphenyls in Human Milk in Rural Colorado." Bulletin of Environmental Contamination and Toxicology 9(4): 222-226.

Savage, E.P., J.D. Tessari, J.W. Malberg, H.W. Wheeler, and J.R. Bagby. 1973b. "Organochlorine Pesticide Residues and Polychlorinated Biphenyls in Human Milk, Colorado-1971-1972." Pesticides Monitoring Journal 7(1): 1-5.

Schmidt, T.T., R.W. Risebrough, and F. Gress. 1971. "Input of Polychlorinated Biphenyls into California Coastal Waters from Urban Sewage Outfalls." Bulletin of Environmental Contamination and Toxicology 6: 235-243.

Seiber, J.N., T.E. Woodrow, T.M. Shafik, and H.F. Enos. 1975. "Determination of Pesticides and their Transformation Products in Air," in Environmental Dynamics of Pesticides: 17-43. Plenum Press, New York and London.

Sernyak, R. 1975. Rollins Environmental Services, Bridgeport, New Jersey. Personal communication.

Shea, K.P. 1973. "PCB." Environment 15(9): 25-28.

Sherma, J. 1975. "Gas-Chromatography Analysis of Polychlorinated Biphenyls and Other Non Pesticide Organic Pollutants." Advances in Chromatography 12: 141-176. Marcel Dekker Inc.

Sinclair, P.R., and S. Granick. 1975. "Uroporphyrin Formation Induced by Chlorinated Hydrocarbons (Lindane, Polychlorinated Biphenyls, Tetrachlorodibenzo-p-Dioxin). Requirements for Endogenous Iron, Protein Synthesis and Drug-Metabolizing Activity." Biochemical and Biophysical Research Communications 61(1): 124-133.

Skrentny, R.F., R.W. Hemken, and H.W. Dorough. 1971. "Silo Sealants as a Source of Polychlorobiphenyl (PCB) Contamination of Animal Feed." Bulletin of Environmental Contamination and Toxicology 6(5): 409-416.

Södergren, A. 1972. "Chlorinated Hydrocarbon Residues in Airborne Fallout." Nature 236: 395-397.

Staiff, D.C., G.E. Quinby, D.L. Spencer, and H.G. Starr, Jr. 1974. "Polychlorinated Biphenyl Emission from Fluorescent Lamp Ballasts." Bulletin of Environmental Contamination and Toxicology 12(4): 455-463.

Stalling, D.L., and F.L. Mayer, Jr. 1972. "Toxicities of PCBs to Fish and Environmental Residues." Environmental Health Perspectives Exp 1: 159-164.

Stanley, C.W., J.E. Barney, M.R. Helton, and A.R. Yobs. 1971 "Measurement of Atmospheric Levels of Pesticides." Environmental Sci. and Technol. 5: 430.

Strik, J.J.T.W.A. 1973. "Chemical Porphyria in Japanese Quail (Conturnix japonica) Enzyme." Journal of Enzyme Physiology and Pathology 16: 211-221.

Sweeny, K.H. 1975. Envirogenics, El Monte California. Personal communication.

Tarrant, K.R., and J.O'G. Tatton. 1968. "Organochlorine Pesticides in Rainwater in the British Isles." Nature 219: 725-727.

Taylor, J. 1975. Gedcor Environmental Protection Corporation, Westland, Michigan. Personal communication.

Tessari, J.D., and D.L. Spencer 1971. "Air Sampling for Pesticides in the Human Environment." Journal of the AOAC 54(6) 1376-1382.

Tomberge, H.F. 1972. "The PCB Situation in Germany." Environmental Health Perspectives Exp.1: 179-180.

Treon, J.F., F.P. Cleveland, J.W. Cappel, and R.W. Atchley. 1956. "The Toxicity of the Vapors of Aroclor 1242 and Aroclor 1254." American Industrial Hygiene Association Quarterly 17 (3): 204-213.

Trout, P.E. 1972. "PCB and the Paper Industry-A Progress Report." Environmental Health Perspectives Exp.1: 63-65.

TRW. 1975. "Summary of CDS Field Testing: Micron and Submicron Process Applications." Redondo Beach, California.

Tucker, E.S., W.J. Litschgi, and W.M. Mees. 1975. "Migration of Polychlorinated Biphenyls in Soil Induced by Percolating Water." Bulletin of Environmental Contamination and Toxicology 13(1): 86-93.

Umeda, G. 1972. "PCB Poisoning in Japan." AMBIO 1: 132-134.

U.S. Army Environmental Hygiene Agency. 1975. "Disposal Instructions for Askarels." USE-ES/WP, 23 October, 1975. Aberdeen Proving Ground, Maryland.

U.S. Department of Health, Education and Welfare. 1972a. "Final Environmental Impact Statement-Rule Making on Polychlorinated Biphenyls." Food and Drug Administration. Sam D. Fine, Associate Commissioner for Compliance.

U.S. Department of Health, Education, and Welfare. 1972b. "News Release." U.S. Food and Drug Administration, Rockville, Maryland. March 17, 1972. (3) proposed regulations (PCBs) limit exposure from foods.

U.S. Environmental Protection Agency. 1972c. "Sewage Sludge Incineration." Task Force of Sewage Sludge Incineration, Washington, D.C. PB-211-323.

U.S. Environmental Protection Agency. 1973a. "Water Quality Criteria 1972" EPA. R3.73.033.

U.S. Environmental Protection Agency. 1973b. "40CFR Part 128, Water Program; Proposed Toxic Pollutant Effluent Standards." Federal Register 38(247): 35388-35395.

U.S. Environmental Protection Agency. 1974 revised. "Analysis of Pesticide Residues in Human and Environmental Samples." Pesticides and Toxic Substances Effects Laboratory. Research Triangle Park, N.C.

Vainio, H. 1974. "Enhancement of Microsomal Drug Oxidation and Glucuronidation in Rat Liver by an Environmental Chemical, Polychlorinated Biphenyl." Chemical and Biological Interactions 9(5): 379-387.

Veith, G.D., and G.F. Lee. 1971. "Chlorobiphenyls (PCBs) in the Milwaukee River." Water Research 5(11): 1107-1115.

Veith, G.D. 1972. "Recent Fluctuations of Chlorobiphenyls (PCBs) in the Green Bay, Wisconsin, Region." Environmental Health Perspectives Exp 1: 51-54.

Venezia, R.A. 1976. U.S. EPA. Personal Communication.

Versar, Inc. 1975a. Task III. Draft Report Contract 68-01-3259. Development of a Study Plan for Definition of PCB Usage, Wastes, and Potential Substitution in the Investment Casting Industry.

Versar, Inc. 1975b. "Substitutes in PCBs Status and Prospects." Personal communication, U.S. EPA.

Villeneuve, D.C., D.L. Grant, K. Khera, D.J. Clegg, H. Baer, and W.E.J. Phillips. 1971. "The Fetotoxicity of a Polychlorinated Biphenyl Mixture (Aroclor 1254) in the Rabbit and in the Rat." Environmental Physiology 1(2): 67-71.

Villeneuve, D.C. L.M. Reynolds, G.H. Thomas, and W.E.J. Phillips. 1973. "Polychlorinated Biphenyls and Polychlorinated Terphenyls in Canadian Food Packaging Materials." Journal of the Association of Official Analytical Chemists 56(4): 999-1001.

Vos, J.G., J.H. Koeman, H.L. van der Maas, M.C. ten Noever de Brauw, and R.H. deVos. 1970. "Identification and Toxicological Evaluation of Chlorinated Dibenzofuran and Chlorinated Naphthalene in Two Commercial Polychlorinated Biphenyls." Food Cosmetics and Toxicology 8(6): 625-633.

Vos, J.G., J.J.T.W.A. Strik, C.W.M. van Holsteijn, and J.H. Pennings. 1971. "Polychlorinated Biphenyls as Inducers of Hepatic Porphyria in Japanese Quail, with Special Reference to Aminolevulinic Acid Synthesis Activity, Fluorescence, and Residues in the Liver." Toxicology and Applied Pharmacology 20(2): 232-240.

Vos, J.G. 1972. "Toxicology of PCBs for Mammals and for Birds." Environmental Health Perspectives, Exp. 1: 105-117.

Wakimoto, T., R. Tachikawa, T. Ogawa, and T. Watanabe. 1974. "Method for the Quantitation of Organic Chlorine Compounds in Air by the Dry Sampling Method." Japan Analyst 23(7): 790-793.

Wallnöfer, P.R., M. Koniger, and O. Hutzinger. 1973. "The Solubilities of Twenty-One Chlorobiphenyls in Water." Analabs, Inc. Research Notes 13(3): 14-16.

Walker, W.H. 1973. "Where Have All the Toxic Chemicals Gone?" Ground Water 11(2): 11-20.

Whitson, F. 1976. TRW, Redondo Beach, California. Personal communication.

Willett, L.B. 1974a. "Coatings as Barriers to Prevent Polychlorinated Biphenyl Contamination of Silage." Journal of Dairy Science 57(7): 816-825.

Willett, L.B. 1974b. "Coatings for Silo Continue to be Effective Barriers to PCBs." In Agricultural Research and Development Center Research Summary 76: 33-36.

Williams, R., and A.V. Holden. 1973. "Organochlorine Residues from Plankton." Marine Pollution Bulletin 4(7): 109-111.

Willmore, C.B. 1976. National Electrical Manufacturers Association Washington, D.C. Personal communication.

Yap, H.H., D. Desaiah, and L.K. Cutkomp. 1971. "Sensitivity of Fish ATPases to Polychlorinated Biphenyls." Nature 233(5314): 61-62.

Yobs, A.R. 1972. "Levels of Polychlorinated Biphenyls in Adipose Tissue of the General Population of the Nation." Environmental Health Perspectives Exp 1: 79-81.

Young, D.R., T.C. Heesen, D.J. McDermott, and P.E. Smokler. 1974. "Marine Inputs of Polychlorinated Biphenyls and Copper From Vessel Antifouling Paints." *Southern California Coastal Water Research Project* TM 212, May.

Young, D.R. 1975. Personal communication.

Young, D.R., and T.C. Heesen. 1975. "Inputs of DDT and PCB." *Southern California Coastal Water Research Project. Annual Report*.

Young, D.R., D.J. McDermott, T.C. Heesen, and J. Tsu-Kai. 1975a. "Pollutant Inputs and Distribution Off Southern California." Preprint of a paper presented at the 169th National Meeting of the American Chemical Society, Philadelphia, Pennsylvania, April 8-10.

Young, D.R., D.J. McDermott, and T.C. Heesen. 1975b. "Polychlorinated Biphenyls Off Southern California." Paper presented at the International Conference on Environmental Sensing and Assessment, September 14-19, Las Vegas, Nevada.

Young, D.R., D.J. McDermott, and T.C. Heesen. 1975c. "Polychlorinated Biphenyl Inputs to the Southern California Bight." Background paper prepared in the National Conference on Polychlorinated Biphenyls, 19-21 Nov. Chicago, Illinois.

Yule, W.N., A.F.W. Cole, and I. Hoffman. 1971. "A Survey for Atmospheric Contamination Following Forest Spraying with Fenitrothion." *Bull. Environ. Contam. Toxicology* 6: 289.

Zitko, V., and P.M.K. Choi. 1971. "PCB and Other Industrial Halogenated Hydrocarbons in the Environment." *Fisheries Research Board of Canada (Technical Report No. 272)*, St. Andrews, N.B.